

**NEAR FIELD RECEIVING WATER MONITORING OF TRACE
METALS IN CLAMS (*MACOMA BALTHICA*) AND SEDIMENTS
NEAR THE PALO ALTO WATER QUALITY CONTROL PLANT
IN SOUTH SAN FRANCISCO BAY, CALIFORNIA: 1999-2001**

U. S. GEOLOGICAL SURVEY

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ABSTRACT

This report presents trace element concentrations analyzed on samples of fine-grained sediments and clams (*Macoma balthica*) collected from a mudflat one kilometer south of the discharge of the Palo Alto Regional Water Quality Control Plant in South San Francisco Bay. This report serves as a continuation of the Near Field Receiving Water Monitoring Study which was started in 1994. The data for 1999 – 2001 are interpreted within that context. Generally, metal concentrations in both sediments and clam tissue samples have been within the range of values produced by seasonal variability. Copper and zinc, however, display a continued decrease, recording the lowest winter maxima concentrations in both sediment and tissue samples in 2001. Yearly average of bioavailable copper, zinc and silver concentrations in 1999-2001 are some of the lowest recorded since monitoring began in 1975. A slight increase in mercury in sediments and selenium in tissue in early 2001 are also observed. These enrichments are believed to be mainly caused by hydrogeologic processes affecting the area although only continued sampling will confirm whether anthropogenic sources influence the concentrations of these elements.

INTRODUCTION

Sampling sediments and benthic organisms in an estuary is a common method used to determine spatial distributions and temporal trends of metal contamination. Sediment particles strongly bind metals, effectively removing them from solution. As a result, sediments may retain metals released to the environment. Thus, concentrations of metals in sediments serve as a record of metal exposure in an estuary, with at least some integration over time. Fluctuations in the record may be indicative of changes in anthropogenic releases of metals into the environment.

Metals in sediments are also indicative of the level of metal exposure of benthic animals in contact with bottom sediments and suspended particulate materials. However, the route through which organisms assimilate bioavailable sediment-bound metal is not well understood. In order to better estimate bioavailable metal exposures, the tissues of the organisms themselves may be analyzed for trace metals. Benthic organisms concentrate most metals to levels higher than those that occur in solution, and therefore, the record of tissue metal concentrations can be a more sensitive indicator of anthropogenic metal inputs than the sediment record. Different species concentrate metals to different degrees. If one species is analyzed consistently, the results can be employed to indicate trace element exposures to the food web of the organism. For example, silver (Ag), copper (Cu) and selenium (Se) contamination, originally observed in clams (*Macoma balthica*) at the Palo Alto mudflat, was later also found in diving ducks, snails, and mussels from that area (Luoma et al., USGS, unpublished data).

Because of the proven value of the above approaches for monitoring near field receiving waters, the California Regional Water Quality Control Board (RWQCB) has described a Self Monitoring Program, with its re-issuance of the National Pollutant Discharge Elimination System (NPDES) permits for South San Francisco Bay dischargers, that includes specific receiving water monitoring requirements. One of the requirements is for inshore monitoring of metals and other specified parameters using the clam *Macoma balthica* and fine-grained sediments. The protocols should also be compatible with or complement the Board's Regional Monitoring Program. Monitoring efforts are to be coordinated with the U. S. Geological Survey's (USGS) 22 years of previous data collected from the site south of the Palo Alto discharge site.

PURPOSE

The purpose of this study is to present trace metal concentrations observed in sediments and clams at an inshore location in South San Francisco Bay. These data and those collected in earlier studies (Luoma et al., 1997) will be used to approach the following objectives:

- Provide data to assess seasonal and year-to-year trends in trace element concentrations in sediments and clams in receiving waters near the Palo Alto Regional Water Quality Control Plant (RWQCP) as designated in the RWQCB's Self-Monitoring Program guidelines.
- Present the data within the context of historical changes inshore in South Bay and within the context of other locations in San Francisco Bay published in the international literature.
- Coordinate inshore receiving water monitoring programs for Palo Alto and provide data compatible with relevant aspects of the Regional Monitoring Program. The near field data will augment the Regional Monitoring Program as suggested by the RWQCB.
- Provide data which could support other South San Francisco Bay issues or programs such as development of sediment quality standards.

STUDY SITE

The Palo Alto site (PA) is located one kilometer south of the intertidal discharge point of the Palo Alto RWQCP (Figure 1). The data reported here are from samples collected in January 1999 through December 2001.

Spatial distributions of metal concentrations near the Palo Alto RWQCP site were described by Thomson et al. (1984) (also reported by Luoma et al., 1991; 1992; 1993; 1995; 1996; 1997; 1998; Wellise et al., 1999). The RWQCP appeared to be the primary source of the elevated metal concentrations at the PA site in spring, 1980, based upon spatial and temporal trends of Cu, Ag and Zn in clams and sediments (Thomson and others, 1984; Cain and Luoma, 1990). Metal concentrations in sediments and clams (especially Cu and Ag) have declined substantially since the original studies, as more efficient treatment processes and source control were employed that significantly reduced metal discharges from the treatment plant (Hornberger et al., 2000). However, frequent sampling within a year was necessary to characterize those trends since there was significant seasonal variability (Cain and Luoma, 1990; Luoma et al., 1985). This report characterizes trends for 1999-2001, employing the methods described in the succeeding section.

Previous reports (Luoma et al., 1995; 1996; 1997; 1998; Wellise et al., 1999) included another study area in addition to the Palo Alto sampling site. This area was located in a region that was influenced by discharge from the San Jose/Santa Clara Water Pollution Control Plant. Samples were collected from this site from 1994 to September 1999. Reference to the SJ site allowed differentiation of local and regional long-term metal trends.

METHODS

The PA site samples were collected from the exposed mudflat at low tide, with hand and shovel. Sediment samples were scraped from the surface oxidized layers (1 -2 cm) of mud. Thus, samples represent recently deposited sediments, or sediments affected by recent chemical reaction with the water column. Sediment samples were immediately taken to the laboratory and sieved through a 100 μm polyethylene mesh with distilled water to remove large grains that might bias interpretation of concentrations. The mesh size was chosen to match the largest grains typically found in the digestive tract of *Macoma balthica*. To provide a measure of bulk sediment characteristics at a site (and thus provide some comparability with bulk sediment determination such as those employed in the Regional Monitoring Program – San Francisco Estuary Institute (SFEI), 1997), the percent of the sediment mass that passed through the sieve was determined. This fraction is termed percent silt/clay in the following discussion. Previous studies have shown little difference between metal concentrations in sieved and unsieved sediments when silt-clay type sediment is dominant at a station. However, where sand-size particles dominate the bed sediment, differences can be substantial. Spatially and temporally, sediments in extreme South San Francisco Bay can vary in their sand content (Luoma et al., 1995; 1996; 1997; 1998; Wellise et al., 1999; also see SFEI, 1997). Where sand content varies, sieving reduces the likelihood that differences in metal concentration are the result of sampling sediments of different character. All sediment data reported herein were determined from the fraction that passed through the sieve ($< 100 \mu\text{m}$). Some differences between the USGS and the Regional Monitoring Program results (SFEI, 1997) reflected the bias of particle size on the latter's data.

The fraction of sediment that did not pass through the sieve was weighed and the percentage of the bulk sample was determined to assess percent sand and percent silt/clay in the sediment. The $<100 \mu\text{m}$

fraction was dried at 60°C, weighed, and then measured into 0.4 to 0.6 gram aliquots in replicates for analysis. The samples were again dried at 60°C before re-weighing and extraction. The replicate subsamples were digested for near-total metal analysis by refluxing in 10 ml of concentrated nitric acid until the digest was clear. This method is comparable with the recommended procedures of US Environmental Protection Agency and with the procedures employed in the Regional Monitoring Program. It also provides data comparable to the historical data available on San Francisco Bay sediments. While near-total analysis does not result in 100% recovery of all metals, recent comparisons between this method and more rigorous complete decomposition show that trends in the two types of data are very similar (Hornberger et al., 1999). After decomposition, samples were evaporated until dry and reconstituted in dilute (5 percent) hydrochloric acid for analysis. The hydrochloric acid matrix was specifically chosen because it mobilizes silver (Ag) into solution through the creation of Ag-chloro complexes. Sediment samples were also subjected to a partial weak acid extraction in 0.5N Hydrochloric acid (HCl), as a crude chemical estimate of bioavailable metal. These subsamples were extracted for 2 hours with 12 ml of acid at room temperature. The extract was pressure filtered through a 0.45 µm membrane filter before analysis. Total organic carbon was determined by difference between total carbon and carbonate, using a total combustion carbon analyzer. Salinity was determined for surface water and the mantle water of clams at the time of collection using a refractometer. Mantle water and surface water salinity were typically within 1 ppt (‰) of each other.

The deposit feeding clam *Macoma balthica* was collected simultaneously with the sediment samples. More than 60 individuals were collected on each sampling occasion. The range of sizes (shell length) was maximized by intensive field sampling, where possible. Animals were returned to the laboratory and held for 48 hours in ocean water diluted to the ambient salinity at the time of sampling, to depurate undigested material from their digestive tracts. After depuration, the individual clams were separated into 1mm size classes. Soft tissues from all of the individuals in a size class were collected to constitute a single sample for analysis. Samples for each date were thus composed of six to thirteen replicate composites, with each composite consisting of 3 to 15 animals of a similar shell length. Animal tissue samples were dried, weighed and refluxed in concentrated nitric acid until the digest was clear. Digests were then dried and reconstituted in dilute (5 percent) hydrochloric acid for trace metal analysis.

Metals analysis was conducted by using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Mercury (Hg) and Se were determined in both sediment and clam tissues by Hydride Atomic Absorption Spectrophotometry. Mercury subsamples were digested at 100° C in aqua regia, re-digested in 10 percent nitric acid plus potassium dichromate and then reduced at the time of the hydride analysis. Selenium subsamples were digested in concentrated nitric and perchloric acids at 200°C and reconstituted in hydrochloric acid.

All glassware and field collection apparatus used were acid washed, thoroughly rinsed in ultra-clean deionized water, dried in a dust-free positive pressure environment, sealed and stored in a dust free cabinet. Quality control was maintained by frequent analysis of blanks, analysis of National Institute of Standards and Technology (NIST) standard reference materials (tissues and sediments) with each analytical run, and internal comparisons with prepared quality control standards. A full QA/QC plan is available upon request. Analyses of NIST reference materials (oyster tissue, San Joaquin soils) were within an acceptable range of certified values reported by NIST or were consistent where the nitric acid digest did not completely decompose the sediment samples (Table 1 and 2). High recoveries for Cd have been observed for the sediment standard. As a result, Cd in sediments for 2000 and 2001 will not be reported until this instrument interference is corrected or until the samples are re-run with conventional atomic absorption spectrometry (AAS). Tables 3-7 show monthly values for all analyses for both sediment and clam samples.

Appendix 1 shows the details of the analyses of sediments. Appendix 2 lists the details of metal analyses of clam tissues. Statistical data indicates size influences on tissue concentrations, and content calculations are reported with their corresponding summary statistics. Analytical data and detection limits also are given for each sample to aid in verification of peaks and trends.

RESULTS AND DISCUSSION

Figure 2 shows the surface water salinity on the dates that samples were collected at the Palo Alto site. Compared to the previous 5 years, high salinity for 1999 and 2001 were recorded indicating relatively low runoff during winter. Salinity did not go below 20 ppt in 2001, the highest wintertime salinity in the past six years. Only 1994 suggested a comparable pattern of low freshwater inflow during the normal wet season. Maximum salinities for 1999-2001 were comparable to other peak salinities in the past five years, with 1994 and 1997 still showing the highest salinity maxima recorded within the past 8 years.

Sediment characteristics of the samples are shown in Figure 3. Percent silt/clay in sediments indicates particle size distributions before sediments were sieved. At Palo Alto, percent silt/clay typically varied from 50 - 100% by weight. Aluminum (Al) concentrations changed directly with the proportion of clay-size (very fine) particles within the 100 μm fraction of the sediment (after sieving). Iron (Fe) concentrations were probably influenced by a combination of seasonal inputs from the watershed and other sediment processes. Percent silt/clay, Al and Fe tended to follow a seasonal cycle of relative increases early in the year then declining to a minimum by September or October. The seasonal trend, especially for Al and Fe concentrations, was typical of that reported earlier for this site by Thompson-Becker et al. (1985). Those authors suggested that fine sediments, accompanied by high Al and Fe concentrations, are dominant during the period of freshwater input (low salinities through April), reflecting annual terrigenous sediment inputs from runoff. Coarser sediments dominated later in the year because the seasonal diurnal winds progressively winnow the fine sediments into suspension through the summer. All indicators showed winnowing had a greater effect in 2001 than in other years.

The seasonal cycles of chromium (Cr), vanadium (V) and nickel (Ni) in sediments are shown in Figure 4. These elements are strongly enriched in some geologic formations within the watershed. The pattern of seasonal change for these metals in 1999 through 2001 were typical of earlier years, with the highest concentrations early in the year (winter maxima) and the lowest concentrations in September-November. In North San Francisco Bay, studies of sediment cores indicated that concentrations of these elements similar to that reported here were derived from natural geologic inputs (Hornberger et al., 1999). However, Cr and Ni also occur in the effluents of the PA RWQCP. The seasonal variability and the similarities among Cr, Ni and V continued to suggest that hydrogeologic processes were the predominant influence on concentrations of these elements.

Copper maintained its seasonal cycling signature, however, a decrease in its total extract concentration in 2001 was evident (Figure 5). Winter maxima peaks were at 41 $\mu\text{g/g}$ as opposed to 50-58 $\mu\text{g/g}$ in previous years. For the first time, Cu in sediments for 2000 and 2001 has fallen well below the effects range-low (ERL) guidelines set by the National Oceanic and Atmospheric Administration (Long et al., 1995). Long et al. (1995) defined values between ERL (Effects Range-Low) and ERM (Effects Range-Median) as concentrations that are occasionally associated with adverse effects (21 - 47% of the time for different metals). Values greater than the ERM were frequently associated with adverse effects (42% - 93% of the time for different metals). It must be remembered, however, that these effects levels were derived mostly from bioassay data and are not literally accurate estimates of

sediment toxicity. The decrease in total Cu in sediments was not so much reflected in the HCl-extract trend although the lowest concentration since 1994 was recorded in September 2001.

Figure 6 shows total and HCl-extractable Zn. Zinc showed an evident decrease in its concentration starting in November 2000, with the 2001 winter maxima falling well below the Zn ERL. This trend was recorded for both total and HCl-extractable Zn. Concentrations of HCl-extractable Ag in sediments did not show the 2000-2001 decrease and maintained the range of concentration that was perceived to be attributable to seasonal cycling of the element (Figure 7). This range was above the established concentration for uncontaminated sediments in San Francisco Bay (Hornberger et al., 1999) but well below the Ag ERL. Sediment concentrations of cadmium (Cd) were slightly elevated from 1997 through 1999 compared to earlier years; although overall concentrations were lower compared to projected biological effects thresholds (1.2 µg/g) (Long et al., 1995) (Figure 8). Also, there appears to be a general decreasing trend over the last three years.

Mercury concentrations in Palo Alto sediment remained consistent with earlier years at an enrichment level typical of the Bay as a whole (0.2 - 0.4 µg/g) (Figure 9). Concentrations of Se in sediments showed a maximum in February 1999 that was more elevated than the corresponding seasonal maxima in previous years. This was followed by relatively low concentrations in 2000 and 2001. The maximum Se concentration observed in PA sediment was comparable to the highest concentrations observed in sediments anywhere in the San Francisco Bay (Hornberger et al., 1999).

Annual mean concentrations (on a calendar year basis) of Cu and Ag in *Macoma balthica* are shown in Figures 10 and 11. Exposures to Cu and Ag, as reflected in clam tissues have been of special interest due to the high concentrations that these metals recorded in the 1970s and 1980s. Trends in these two metals at Palo Alto were lower throughout the 1990s than in the years prior to 1988. The previous minimum concentrations were observed in 1991, but a five-year period of slightly increased concentrations followed. Since 1997, both Cu and Ag concentrations have shown a period of decline, with 2001 concentrations among the lowest observed during the 20-year period of study.

Copper concentration in clams displayed a seasonal signal, however, the last four years of data evidently showed a decrease in winter maxima (Figure 12). This trend seemed to have started in mid-1997 wherein the range of Cu concentrations decreased to only 17-48 µg/g as opposed to 21-100 µg/g in previous years. Silver also showed the same depressed winter maxima which started in 1997 (Figure 13).

Figures 14-16 show Zn, Cr and Ni concentrations in *Macoma balthica*. Wellise et al. (1999) observed that the metals trends in Palo Alto clam samples were similar to those from the San Jose site, suggesting that regional-scale processes may be more important than treatment plant inputs in controlling seasonality and bioavailability of these elements. The seasonality signal continued in the data from 1999 to 2001 wherein the lowest Cr, Ni, and Zn were observed during Spring (May-June), whereas the maxima typically occurred during winter (December-March). However, Cr and Ni displayed narrower concentration ranges in their 1999-2001 annual cycles due to a slightly depressed winter maxima when compared with previous years. Conversely, one of the highest Zn levels recorded was in March 2000 although the lowest Zn concentration in the entire time series was in November of the same year.

Selenium concentrations in sediments and clam tissue did not show similar trends (Figure 17). While a slight decrease in Se average concentration in sediment was observed for 2000-2001, concentrations in clams varied from <3 µg/g to 7 µg/g, with the highest concentration recorded in January 2001. The cause for the increase in Se concentrations in clam samples is still unclear at this point. On the other hand, Hg in clam samples remained within the concentration range of the element (0.15-0.36 µg/g) since a recorded decrease in mid-1996 (Figure 18).

Figure 19 shows the condition index for clams for the period of 1988 through 2001. Condition index (CI) is a measure of physiological "fatness", the tissue weight of a clam of a given length. It is an index of the clams' well-being and indicative of how well clams prepare for the seasonal reproductive cycle. Seasonally, a clam of a given shell length will add glycogen and weight as it prepares for reproduction. That glycogen is metabolized and weight is lost during and after reproduction. Stress caused by pollutant exposure, salinity stress or lack of food, can consume energy, affect net glycogen accumulation, and reduce condition index.

The condition index for 1999 and 2001 were similar to the period from 1994 through 1996 and even slightly higher values observed in 2000 (Figure 19). High CI in 1997 and 1998 at PA coincided with reduced concentrations of Cu and Ag, as well as a large phytoplankton bloom occurrence (Wellise et al., 1999). Moreover, while CI maxima were typically within the range of values observed in previous years, the annual minima for 1999-2001 have been the highest in the 14-year dataset. This may be suggestive of further improvement in clam physiology, however, further investigation is necessary to understand the dynamics of food availability and condition to interpret this observation. A simple correlation between maximum condition index and the preceding months' maximum metal exposure was not significant. Still, the data distribution (Figure 20) raised the possibility that Cu concentrations above 80 - 90 $\mu\text{g/g}$ might affect growth in the bivalves. The 1999-2001 data were consistent with this relationship since the copper concentrations are below the threshold where it has a probable effect on habitat conditions.

Frequent sampling was essential for characterizing ambient metal concentrations in the environments in the vicinity of the outfall. Monitoring studies could not always unambiguously determine the causes of the trends in metals concentrations in either sediments or clams. The value of monitoring was to describe trends, to identify previously undocumented phenomena, and to raise otherwise unrecognized hypotheses that might guide detailed explanatory studies. Signals coming from anthropogenic sources overprinted onto natural annual and inter annual variability could only be recognized through the interpretation of time series data. For many elements of regulatory interest, including Cr, V, Ni, and Zn, regional scale factors appeared to influence sedimentary and bioavailable concentrations, although this may not be completely accurate in all years. The decrease in Cu and Ag concentrations in clam and sediment samples reflected the continued decrease in these metals' loading from the treatment plant. However, other variables that may contribute to this decline in concentration such as a decrease in precipitation for 1999-2001 should still be investigated.

REFERENCES CITED

- Cain, D. J. and Luoma, S. N., 1990, Influence of seasonal growth, age and environmental exposure on Cu and Ag in a bivalve indicator, *Macoma balthica* in San Francisco Bay: Marine Ecology Progress Series 60, p. 45 - 55.
- Hornberger, M. I., Luoma, S. N., Van Geen, A., Fuller, C. C., and Anima, R. 1999, Historical trends of metals in the sediments of San Francisco Bay, California. Marine Chemistry 64, p. 39-55.
- Hornberger, M.I., Luoma, S. N., Cain, D., Parchaso, F., Brown, C., Bouse, R., Wellise, C.J., Thompson, J., 2000, Bioaccumulation of metals by the bivalve *Macoma balthica* at a site in South San Francisco Bay between 1977 and 1997: Long-term trends and associated biological effects with changing pollutant loadings. U. S. Geological Survey Open File Report 99-55. Menlo Park, California.
- Long, E. R., MacDonald, D. D., Smith, S. L., and Calder, F. D., 1995, Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments: Environmental Management, v. 19, p. 81 - 97.
- Luoma, S. N., Cain, D. J., Brown, C. and Axtmann, E. V., 1991, Trace Metals in Clams (*Macoma balthica*) and sediments at the Palo Alto Mudflat in South San Francisco Bay: April, 1990 - April, 1991. U. S. Geological Survey Open File Report 91-460. Menlo Park, California. 47pp.
- Luoma, S. N., Cain, D. J., Brown, C. and Hornberger, M., 1992, Trace Metals in Clams (*Macoma balthica*) and sediments at the Palo Alto Mudflat in South San Francisco Bay: May 1991 - May 1992. U. S. Geological Survey Open File Report 92-456. Menlo Park, California. 51pp.
- Luoma, S. N., Cain, D. J., Brown, C. and Hornberger, M., 1993, Trace Metals in Clams (*Macoma balthica*) and sediments at the Palo Alto Mudflat in South San Francisco Bay: June 1992 - June 1993. U. S. Geological Survey Open File Report 93-500. Menlo Park, California. 52pp.
- Luoma, S. N., Cain, D. J., Brown, C. and Hornberger, M., 1995, Near Field Receiving Water Monitoring of Trace Metals in Clams (*Macoma balthica*) and sediments near the Palo Alto and San Jose/Sunnyvale Water Quality Control Plants in South San Francisco Bay: June 1993 - October 1994. U. S. Geological Survey Open File Report 95-299. Menlo Park, California. 83pp.
- Luoma, S. N., Cain, D. J., Brown, C., Hornberger, M., and Bouse, R. 1996, Near Field Receiving Water Monitoring of Trace Metals in Clams (*Macoma balthica*) and sediments near the Palo Alto and San Jose/Sunnyvale Water Quality Control Plants in South San Francisco Bay: December 1994 - December 1995 U. S. Geological Survey Open File Report 96-203. Menlo Park, California. 90pp.
- Luoma, S. N., Cain, D. J., Brown, C., Hornberger, M., and Bouse, R. 1997, Near Field Receiving Water Monitoring of Trace Metals in Clams (*Macoma balthica*) and sediments near the Palo Alto and San Jose/Sunnyvale Water Quality Control Plants in South San Francisco Bay: 1996 U. S. Geological Survey Open File Report 97-585. Menlo Park, California. 91pp.

- Luoma, S. N., Wellise, C, Cain, D. J., Brown, C., Hornberger, M., and Bouse, R. 1998, Near Field Receiving Water Monitoring of Trace Metals in Clams (*Macoma balthica*) and sediments near the Palo Alto and San Jose/Sunnyvale Water Quality Control Plants in South San Francisco Bay: 1997 U. S. Geological Survey Open File Report 98-563. Menlo Park, California. 88pp.
- San Francisco Estuary Inst. 1997, RMP, Regional Monitoring Program for Trace Substances: 1996. Richmond, CA. 349 pp.
- Thomson, E. A., Luoma, S. N., Johansson, C. E., and Cain, D. J., 1984, Comparison of sediments and organisms in identifying sources of biologically available trace metal contamination: Water Research, v. 18, p. 755 - 765.
- Thomson-Becker, E. A., and Luoma, S. N., 1985. Temporal fluctuations in grain size, organic materials and iron concentrations in intertidal surface sediment. Hydrobiologia, v. 129, p. 91-109.
- Wellise, C., Luoma, S. N., Cain, D. J., Brown, C., Hornberger, M., and Bouse, R. 1999, Near Field Receiving Water Monitoring of Trace Metals in Clams (*Macoma balthica*) and sediments near the Palo Alto and San Jose/Sunnyvale Water Quality Control Plants in South San Francisco Bay: 1998 U.S. Geological Survey Open File Report 99-455. Menlo Park, California. 101pp.

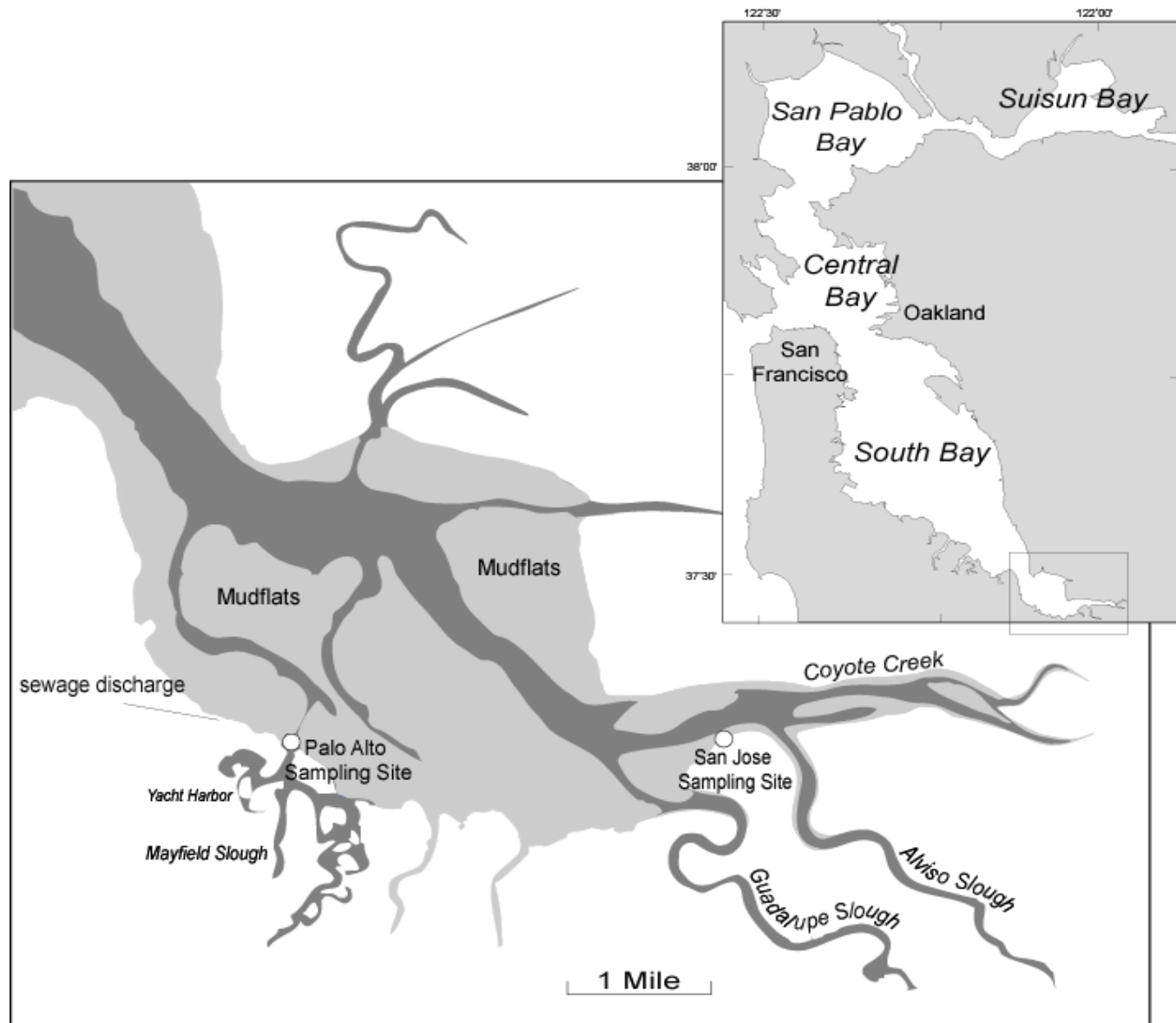


Figure 1. Location of the Palo Alto sampling station in South San Francisco Bay.

Figure 2. Water column salinity at Palo Alto from 1994 through 2001.

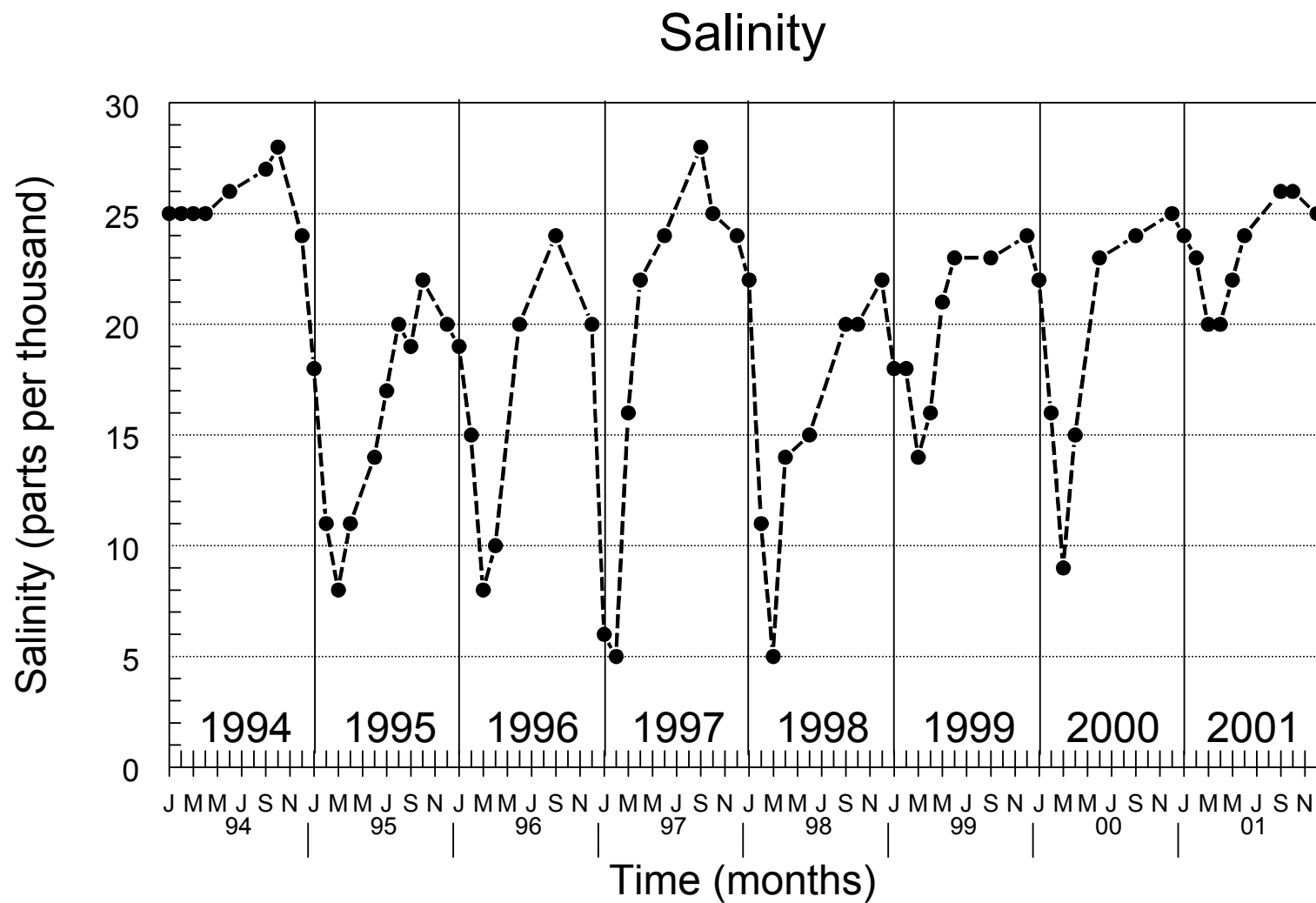


Figure 3. Percent silt/clay, iron and aluminum in sediments at Palo Alto from 1994 through 2001.

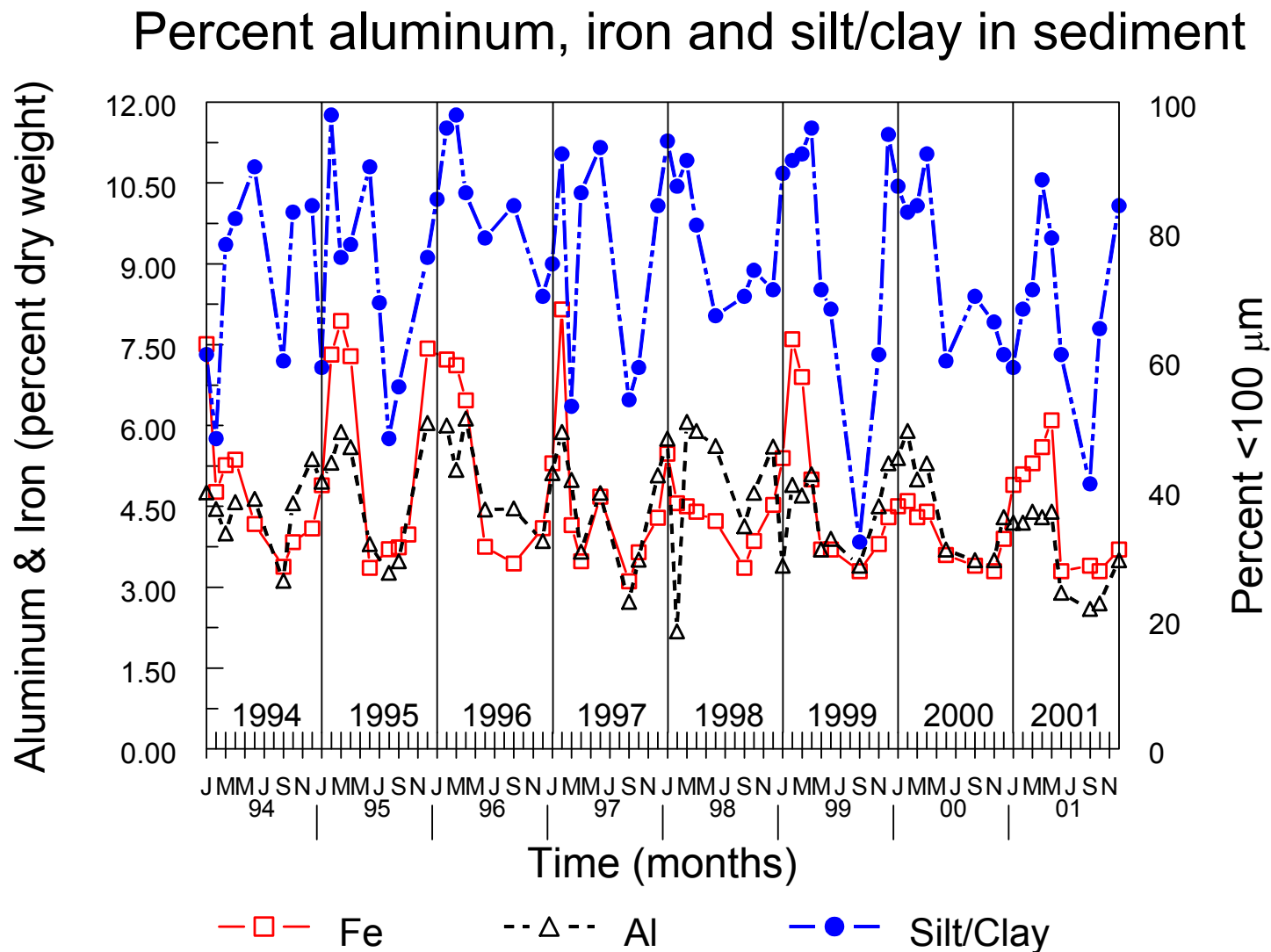


Figure 4. Near-total extraction concentrations of chromium, vanadium, and nickel in sediments at Palo Alto from 1994 through 2001.

Chromium, vanadium, and nickel in sediment

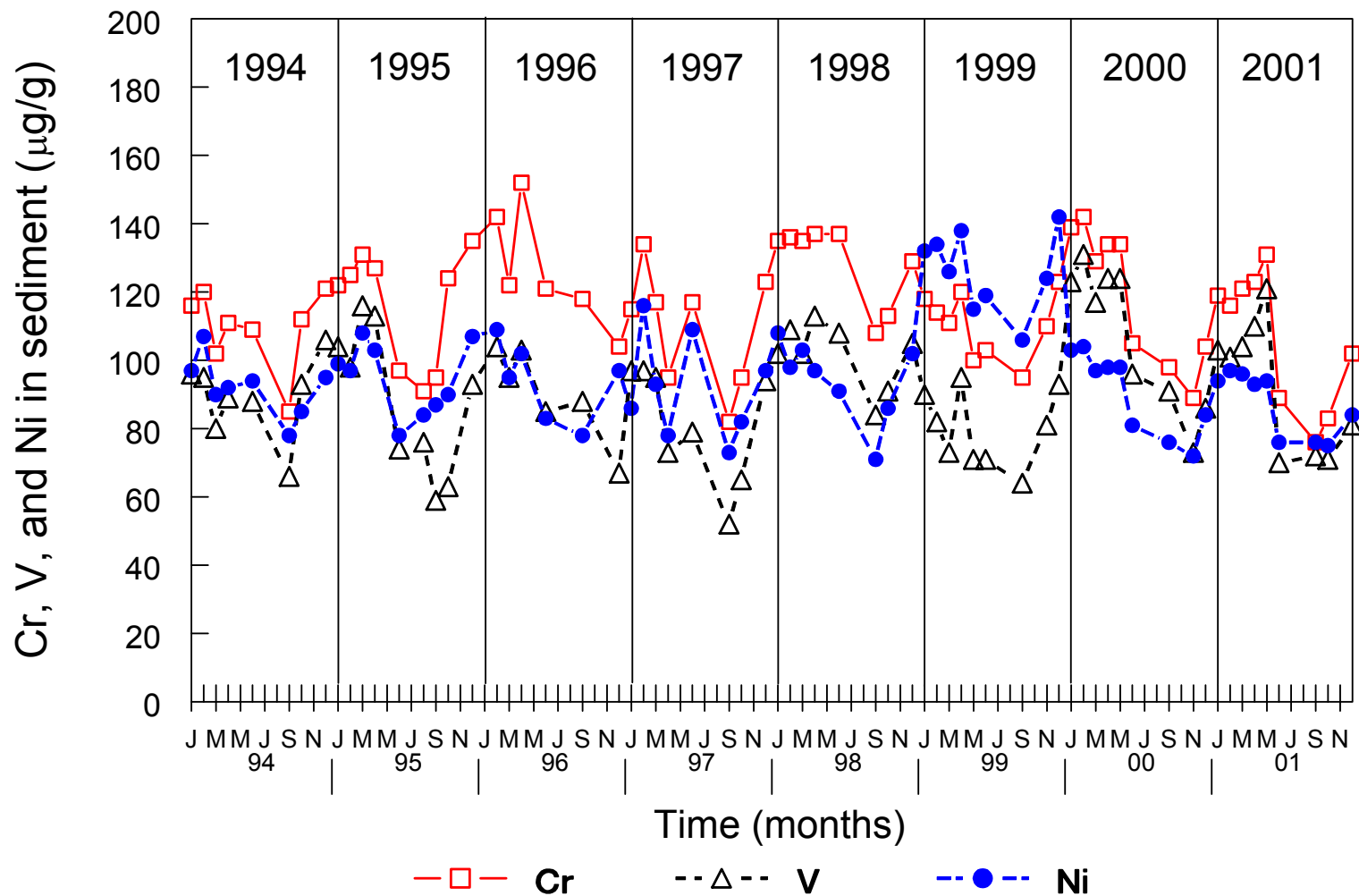


Figure 5. Near-total and acid-extractable copper concentrations in sediments at Palo Alto from 1977 through 2001.

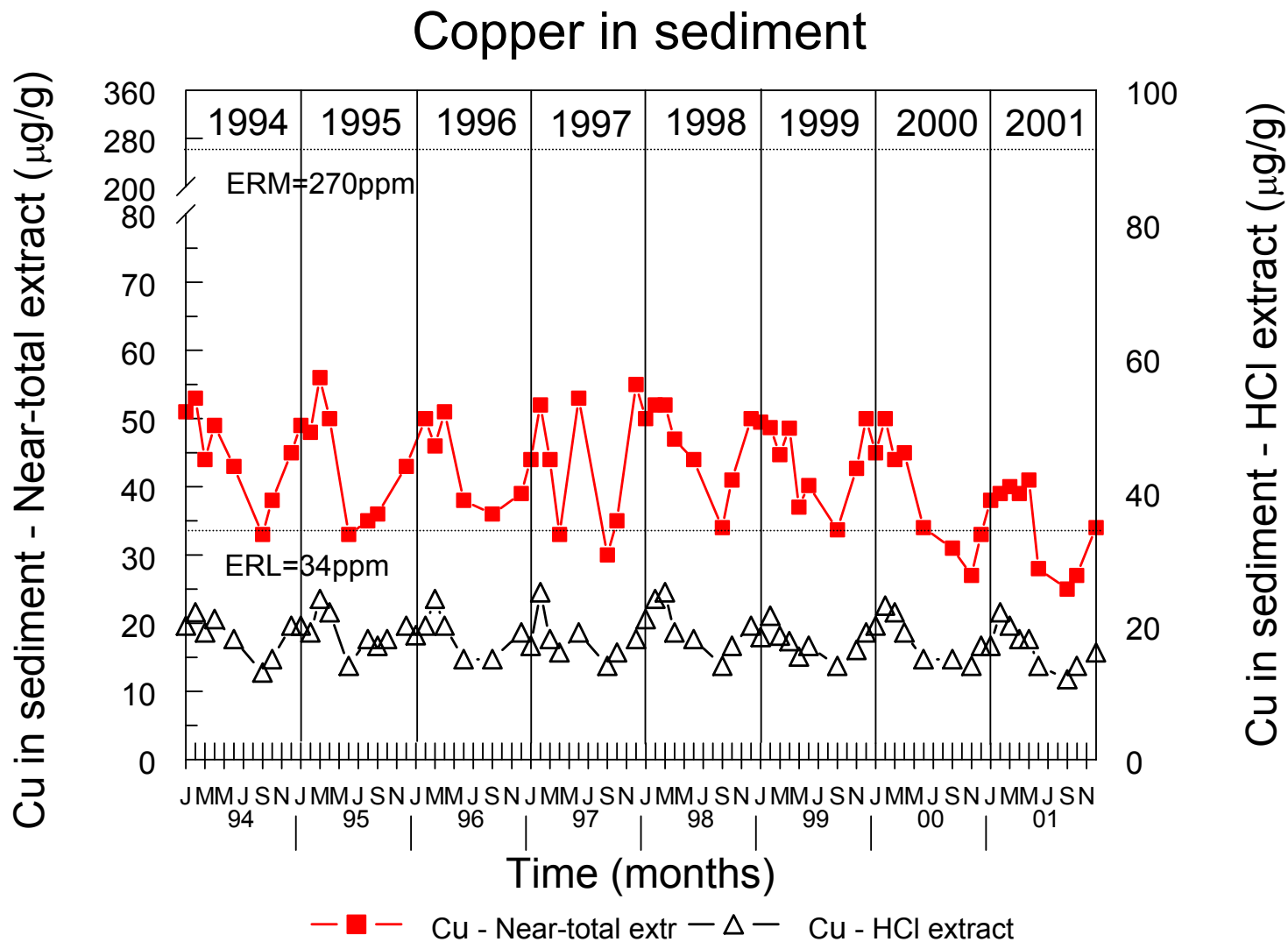


Figure 6. Concentrations of near-total and acid-extractable zinc in sediments at Palo Alto from 1994 through 2001.

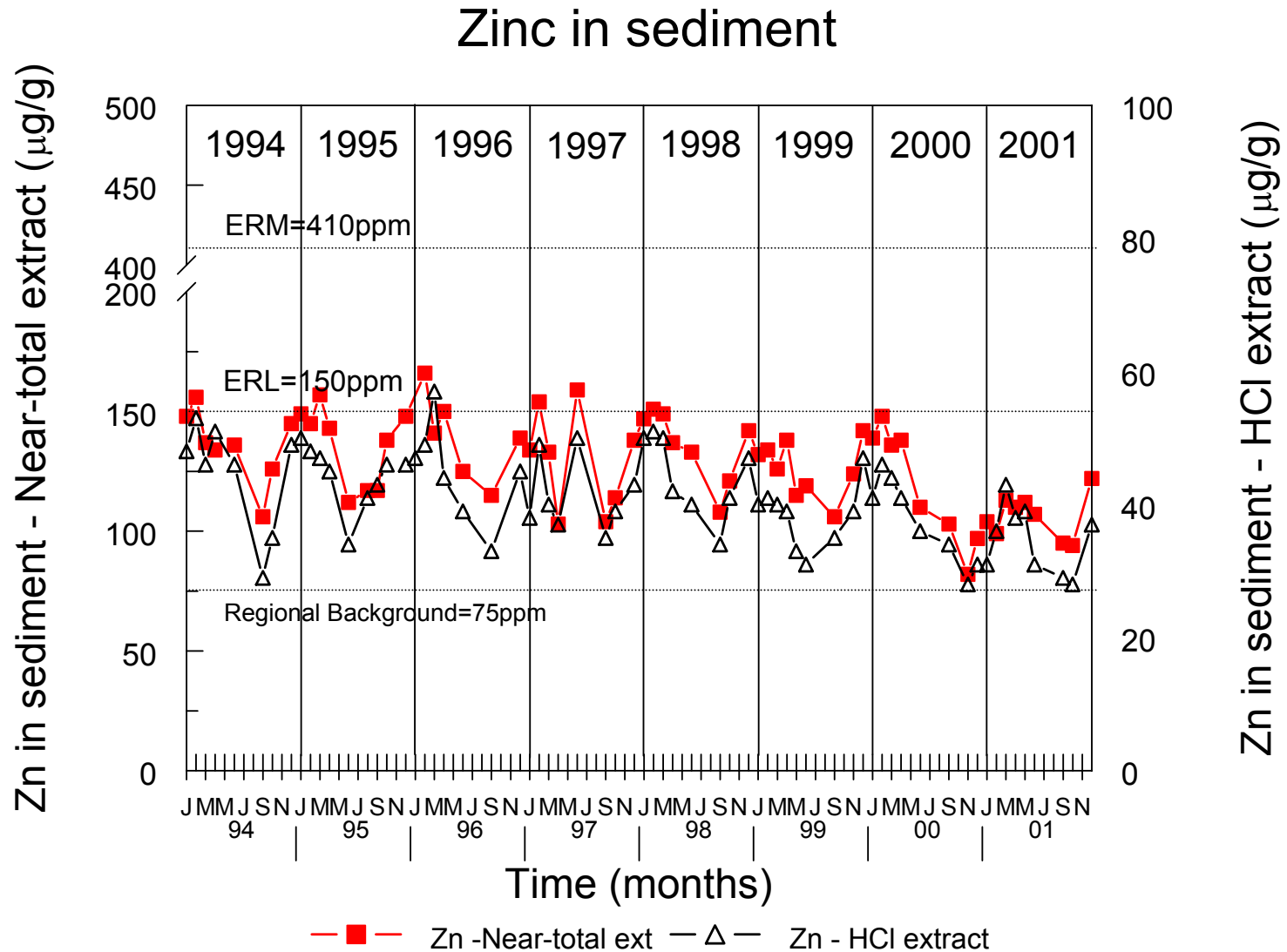


Figure 7. Acid-extractable silver concentrations in sediments at Palo Alto from 1990 through 2001. Extractions were conducted with 0.6 N Hydrochloric acid.

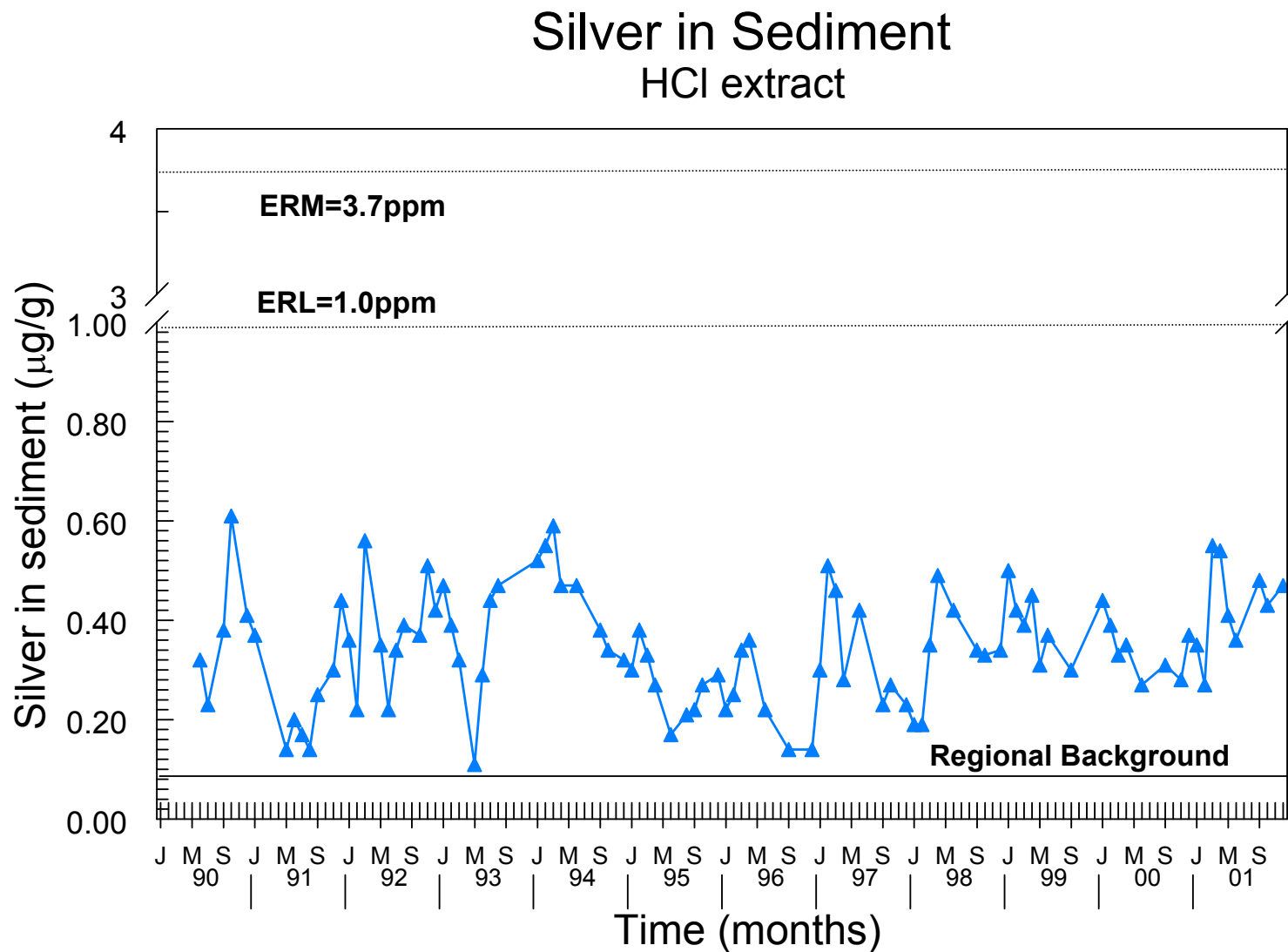


Figure 8. Total extraction concentrations of cadmium in sediments at Palo Alto from 1994 through 1999.

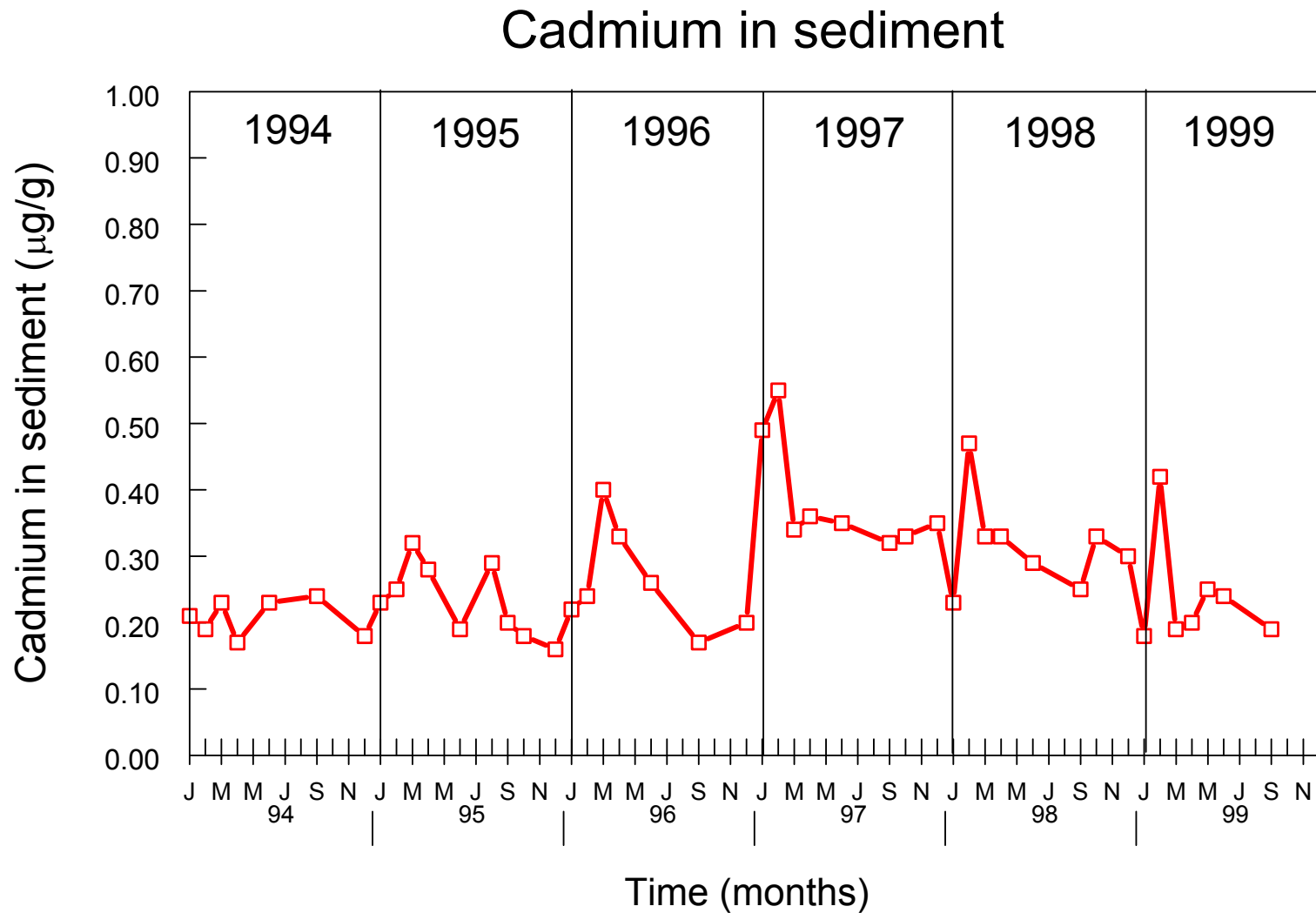


Figure 9. Concentrations of selenium and mercury in sediments at Palo Alto from 1994 through 2001.

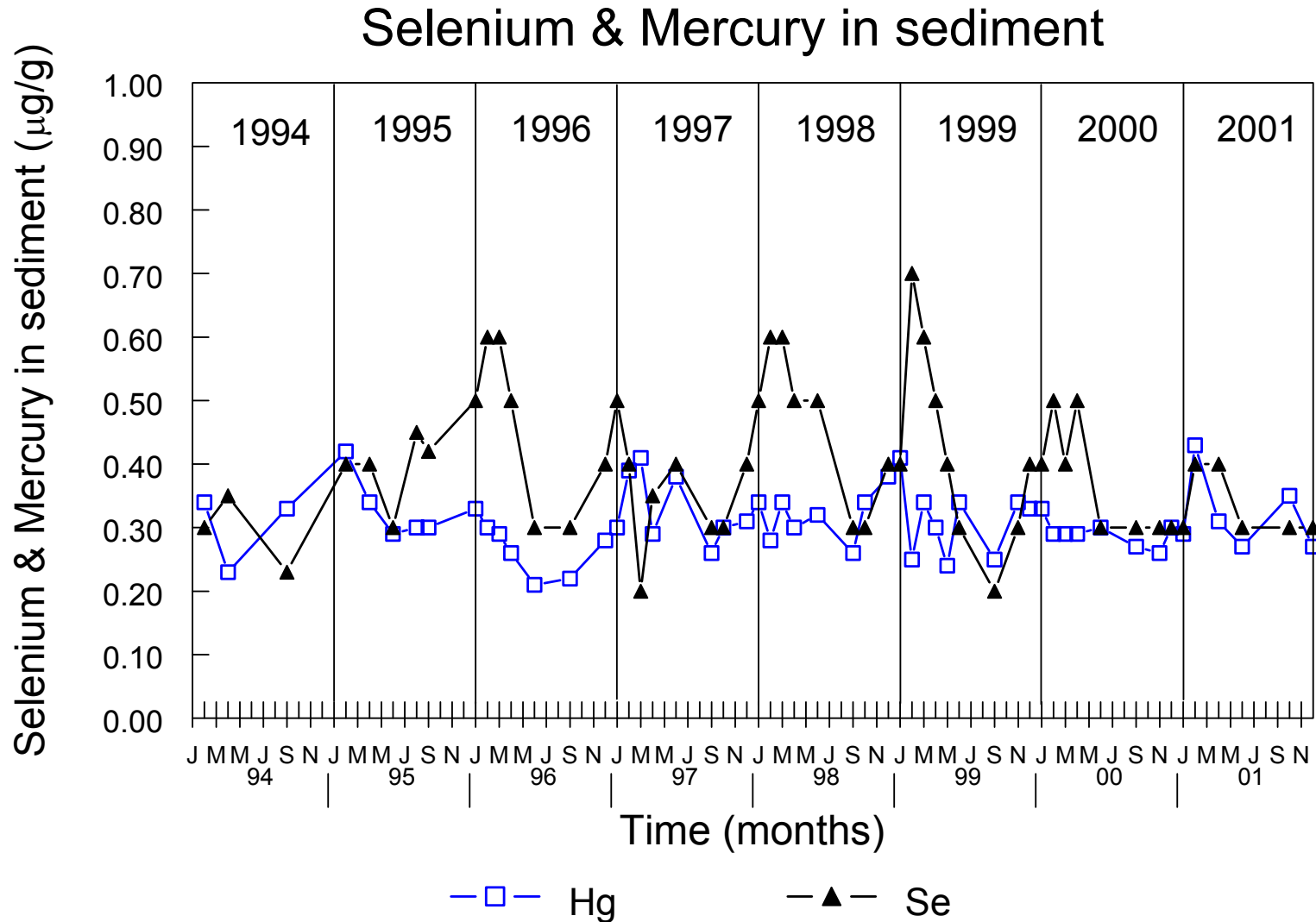


Figure 10. Annual mean concentrations of copper in the clam *Macoma balthica* at Palo Alto from 1977 through 2001. Error bars denote the standard error of the mean (SEM).

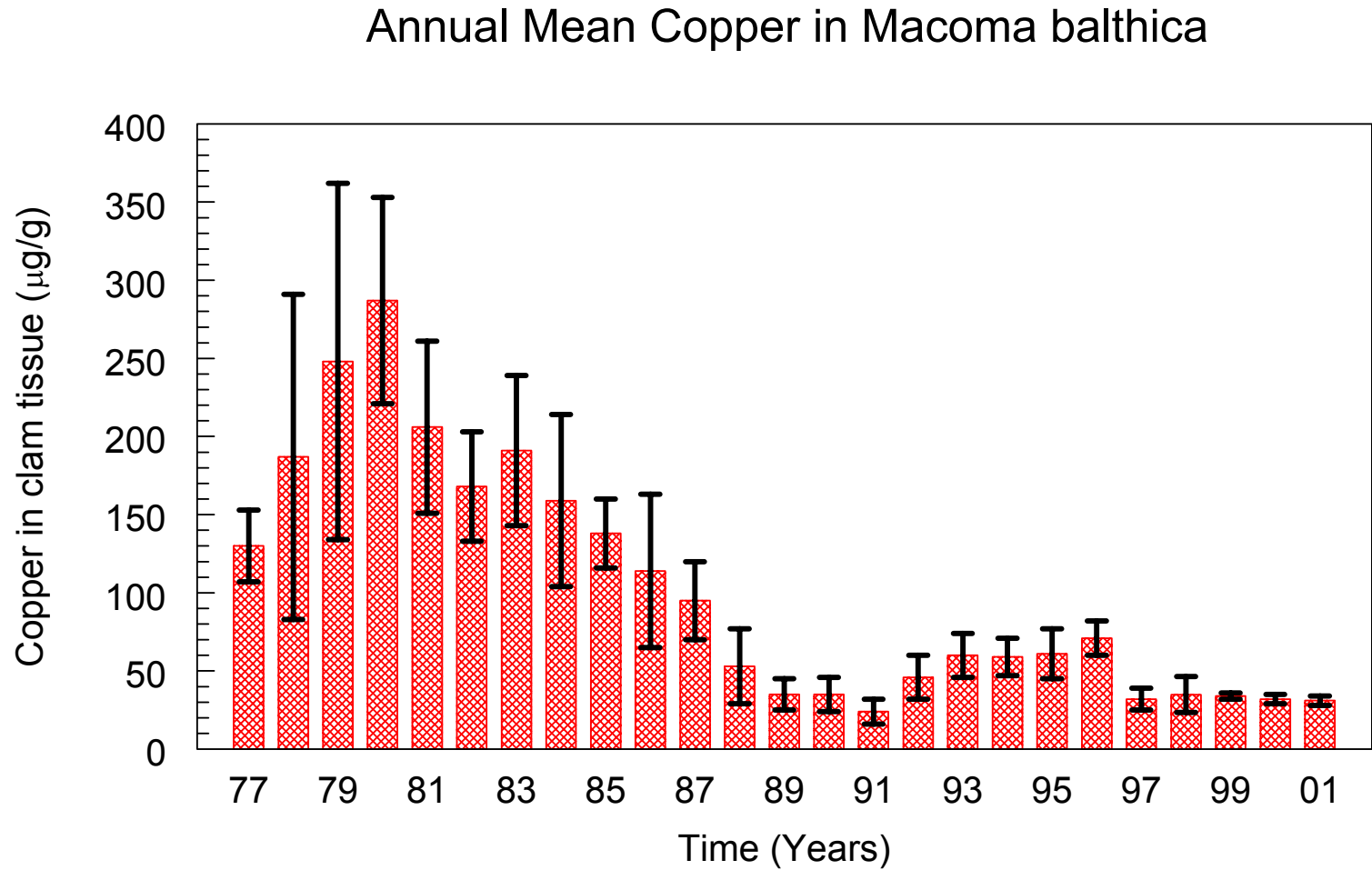


Figure 11. Annual mean concentrations of silver in the clam *Macoma balthica* at Palo Alto from 1977 through 2001. Error bars denote the standard error of the mean (SEM).

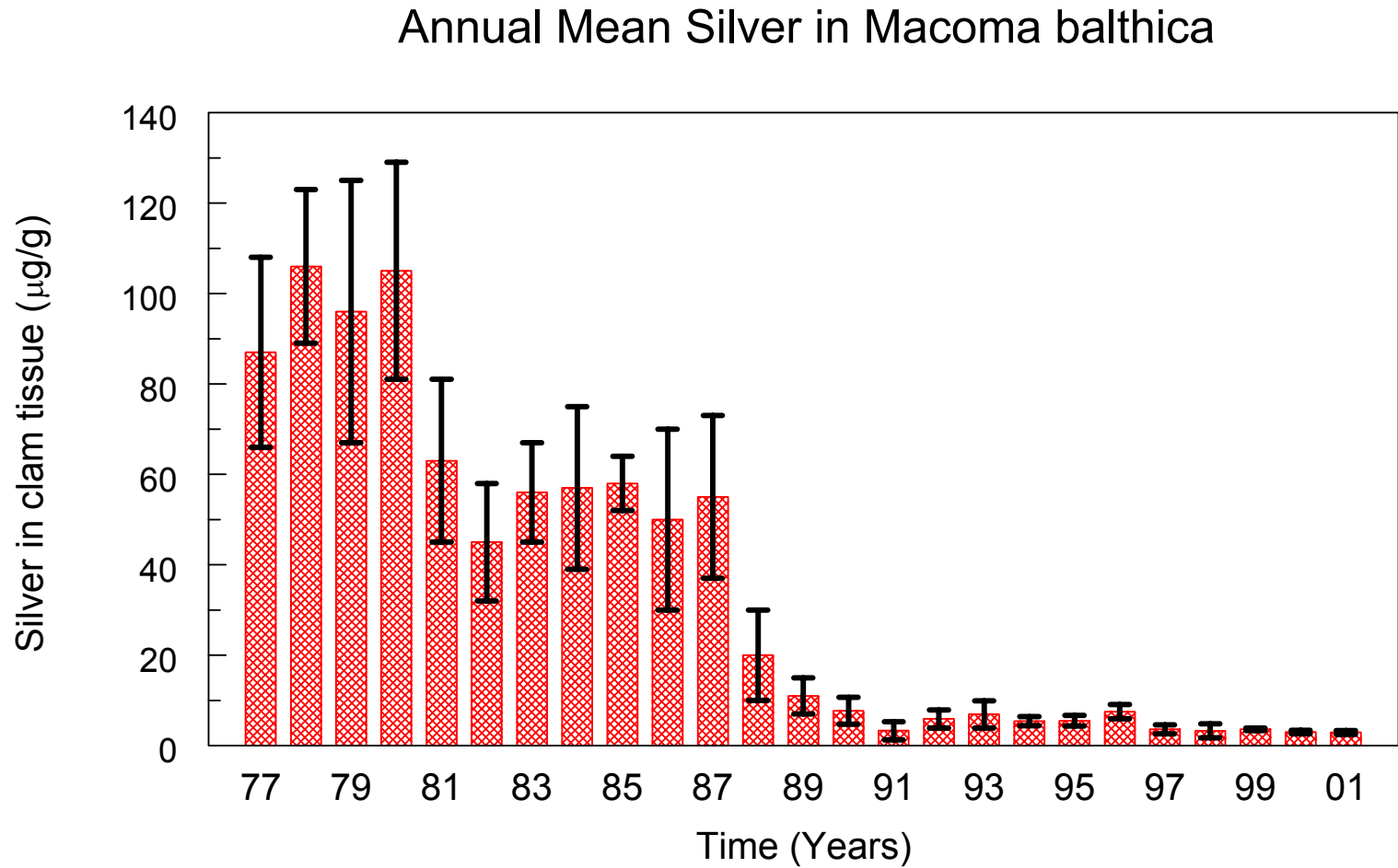


Figure 12. Concentrations of copper in clams (*Macoma balthica*) at Palo Alto from 1994 through 2001. Error bars denote the standard error of the mean (SEM).

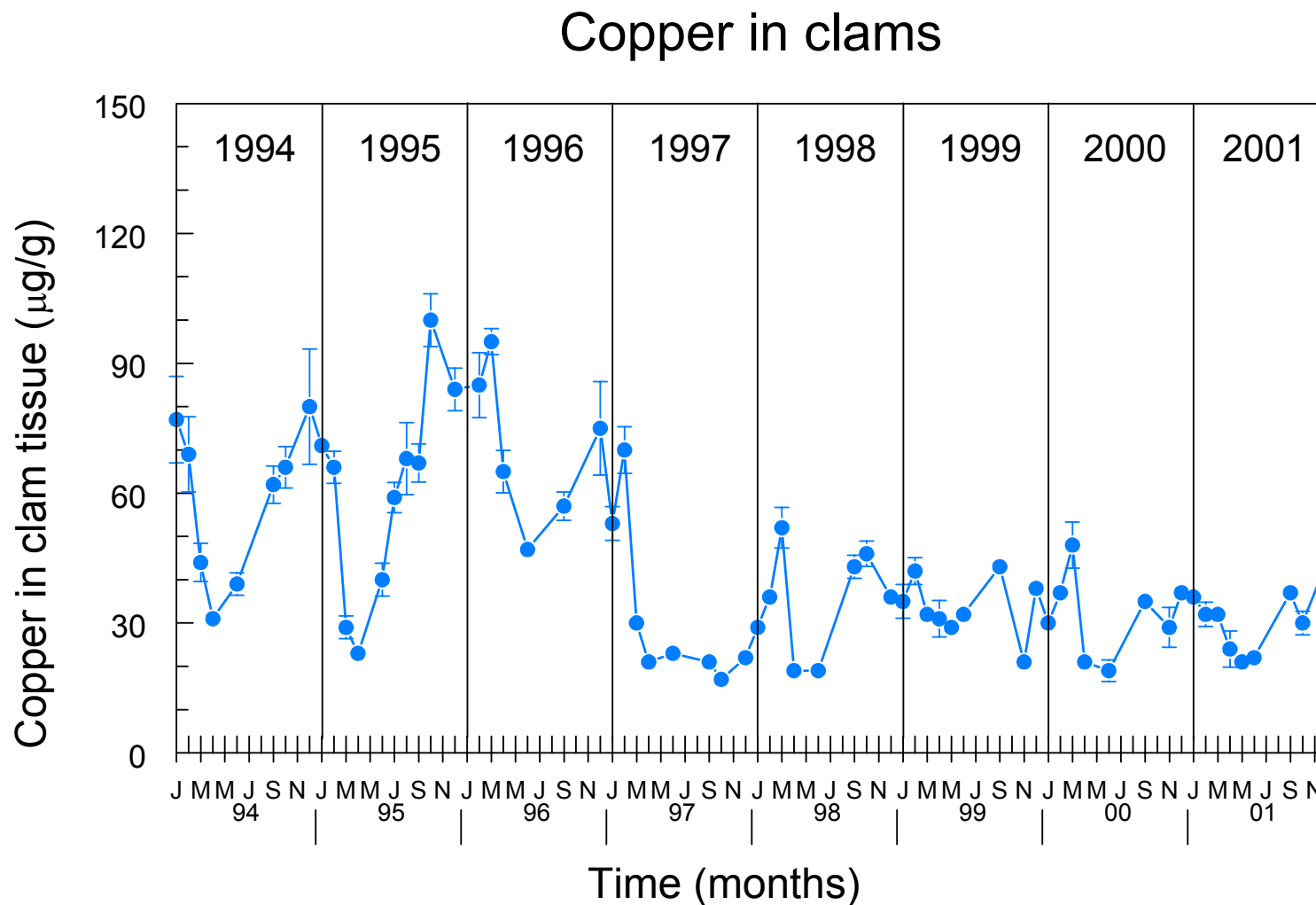


Figure 13. Concentrations of silver in clams (*Macoma balthica*) at Palo Alto from 1994 through 2001. Error bars denote the standard error of the mean (SEM).

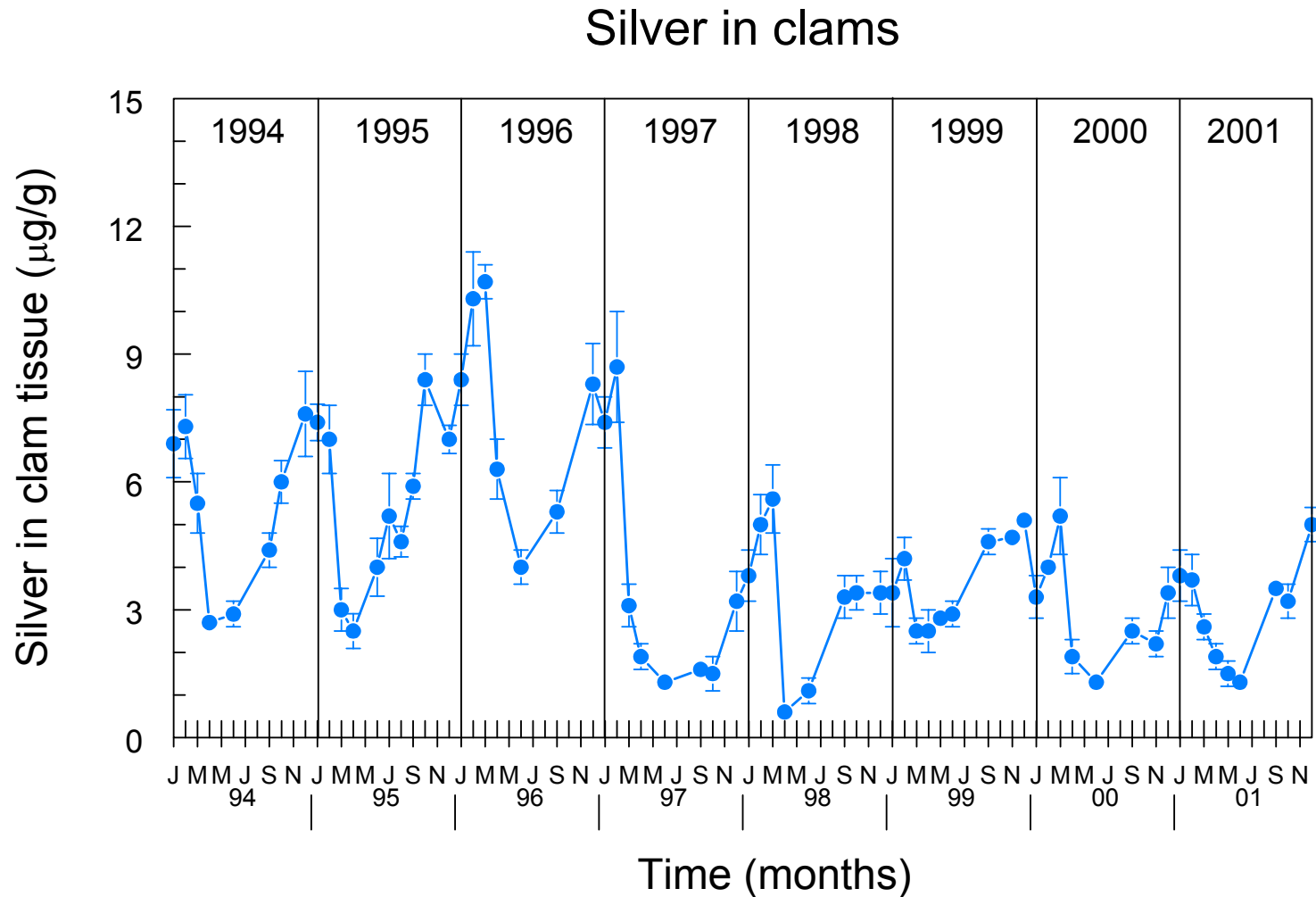


Figure 14. Concentrations of zinc in clams (*Macoma balthica*) at Palo Alto from 1994 through 2001. Error bars denote the standard error of the mean (SEM).

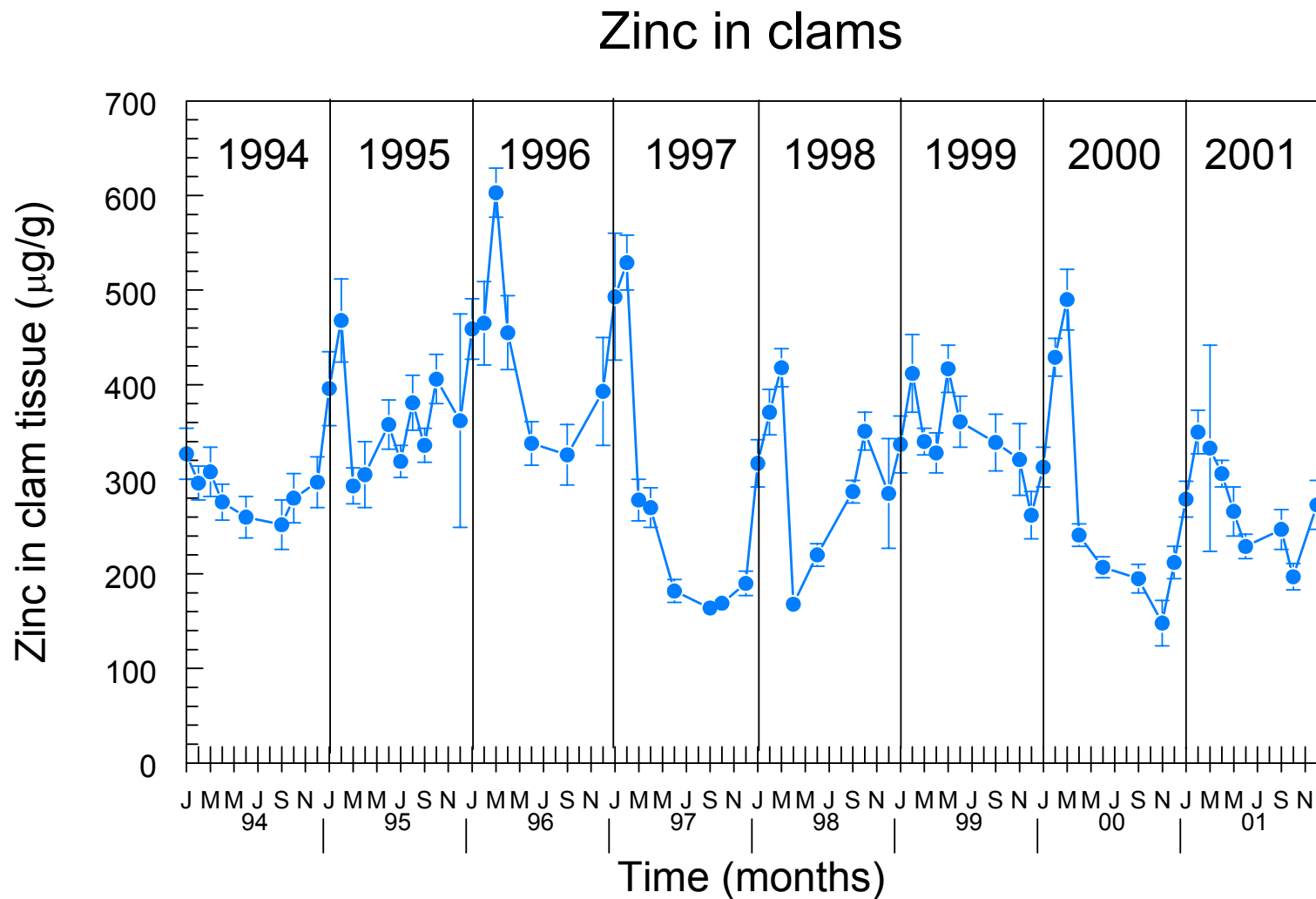


Figure 15. Concentrations of chromium in clams (*Macoma balthica*) at Palo Alto from 1994 through 2001. Error bars denote the standard error of the mean (SEM).

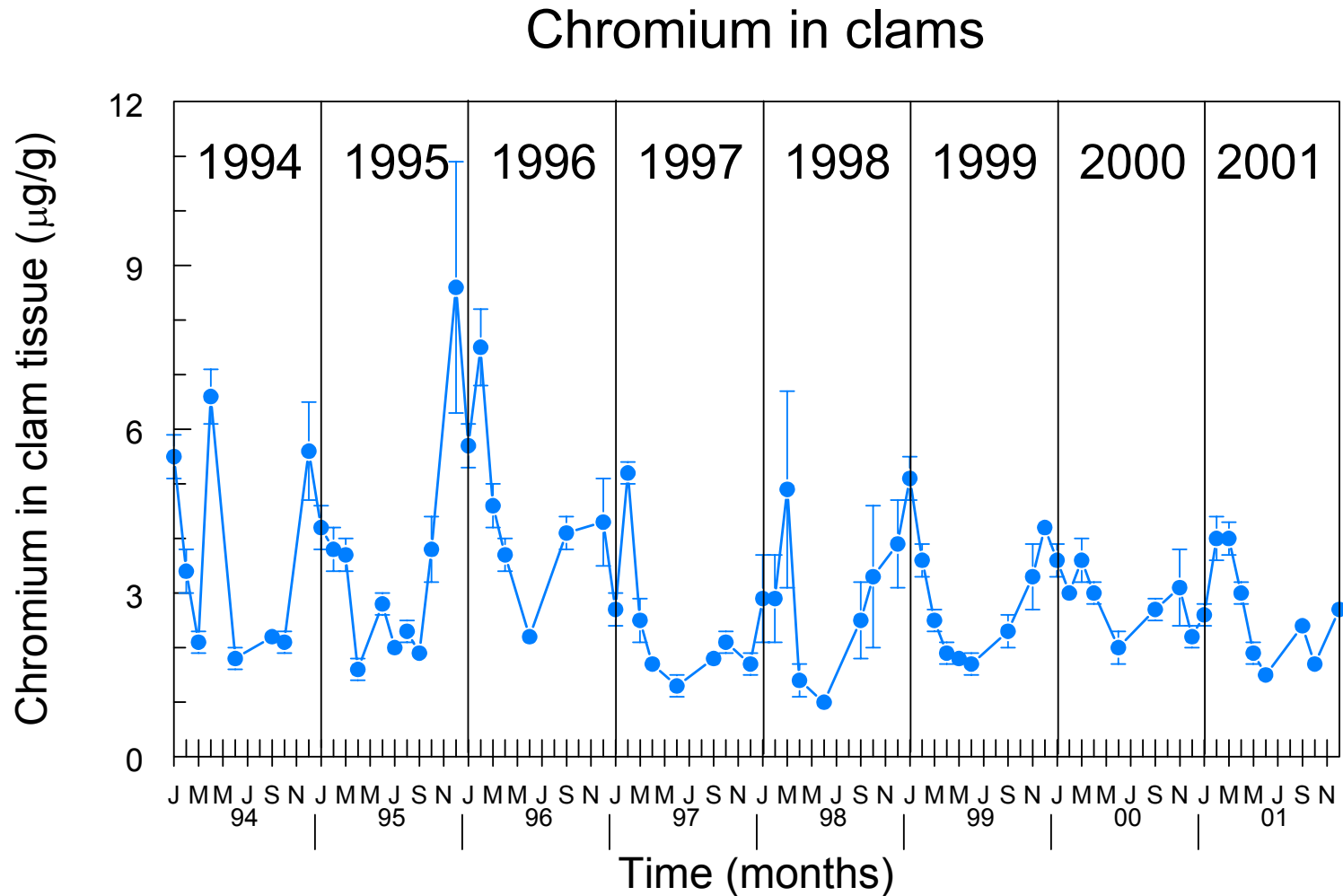


Figure 16. Concentrations of nickel in clams (*Macoma balthica*) at Palo Alto from 1994 through 2001. Error bars denote the standard error of the mean (SEM).

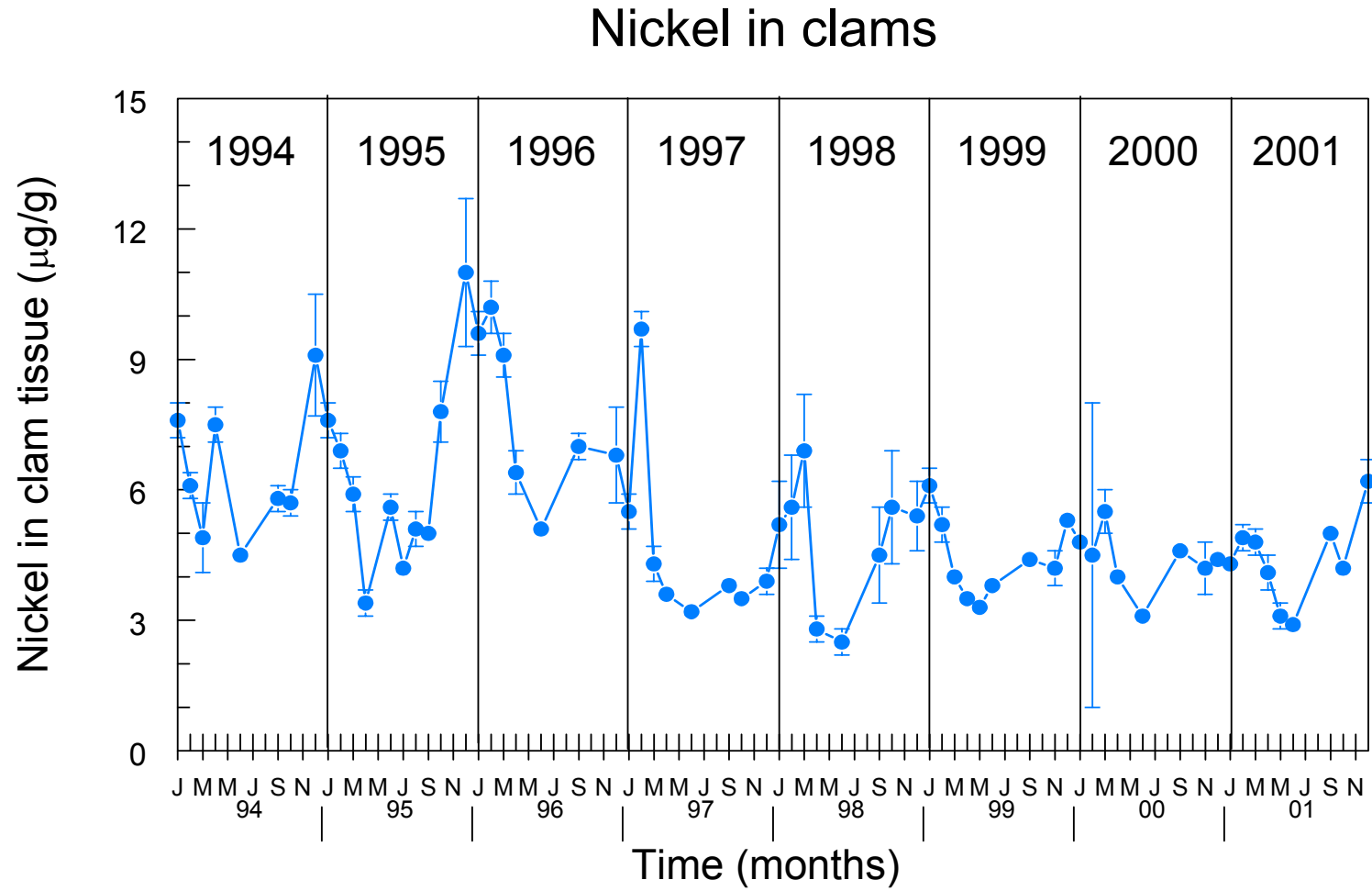
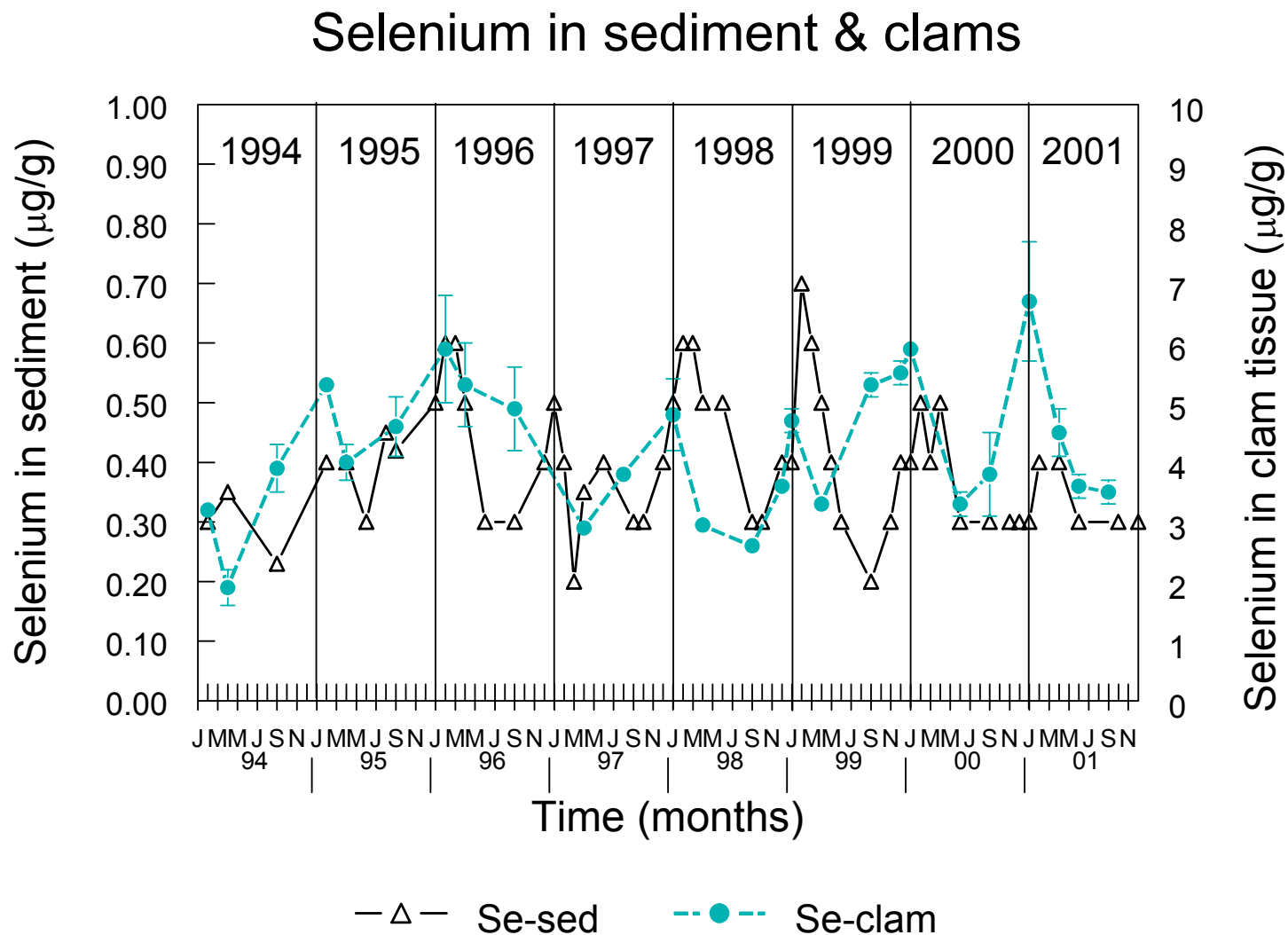


Figure 17. Concentrations of selenium in sediments and clams at Palo Alto from 1994 through 2001. Error bars denote the standard error of the mean (SEM).



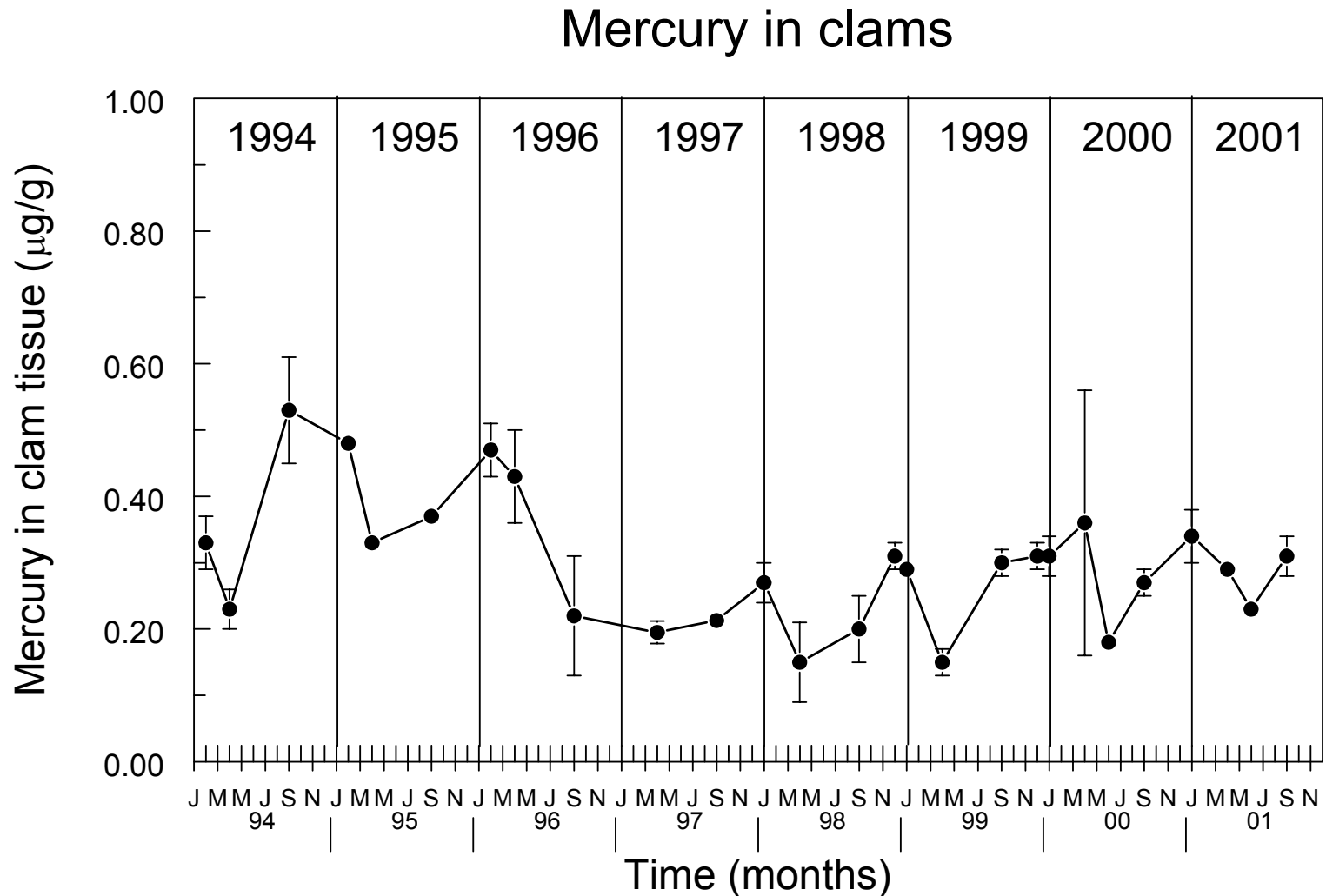


Figure 19. Weight of *Macoma balthica* of 25 mm shell length (condition index) as determined between 1988 through 2001 at Palo Alto.

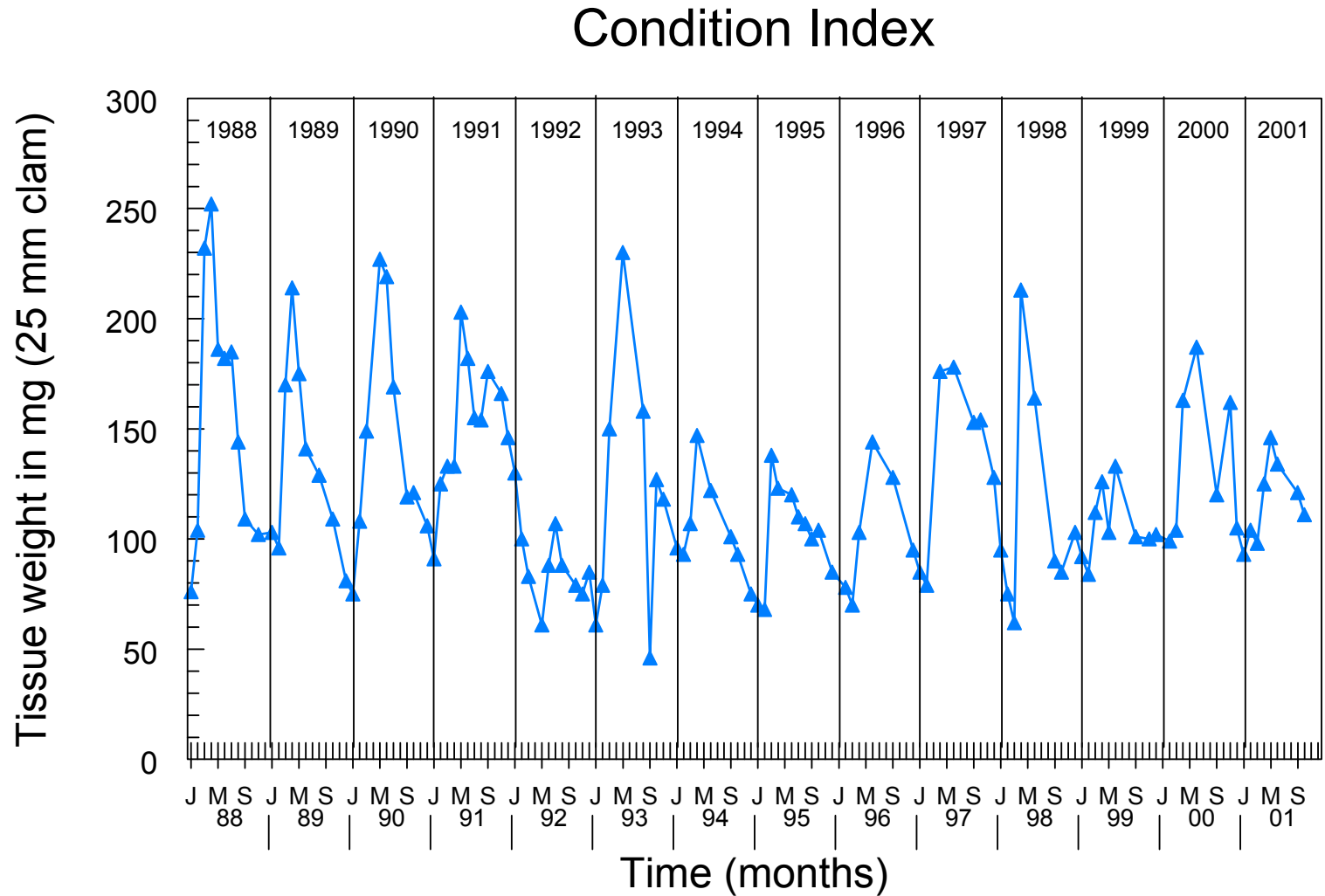


Figure 20. Correlation of maximum condition index in *Macoma balthica* vs. maximum copper concentrations in the months preceding the determination of maximum condition. Data from Palo Alto and San Jose sites for the period from 1990 through 2001.

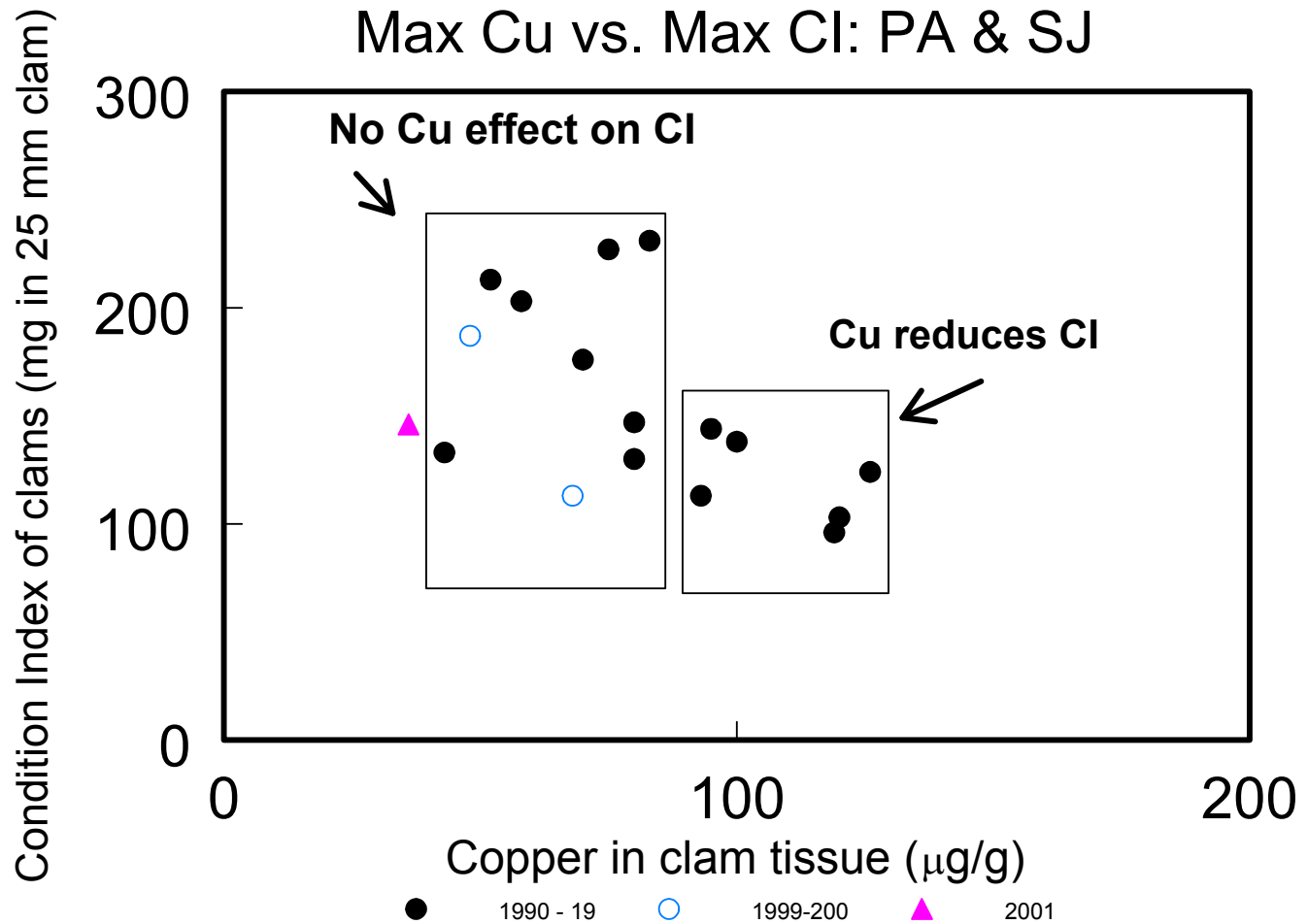


Table 1A. 2000 SRM 2709 (San Joaquin Soil) Recoveries (HNO₃ Extraction)

Month	Rep	Concentration, ug/g								
		AL	CR	CU	FE	MN	NI	PB	V	ZN
January	1	35520	86.1	26.7	30068	482	74.8	15.2	90.5	87.6
	2	35231	85.7	28.8	30018	481	75.4	16.3	94.2	88.2
February	1	36644	86.2	26.7	30110	475	75.1	15.4	93.6	85.5
	2	34954	82.4	24.8	29191	469	74.3	14.3	88.6	83.6
March	1	35762	83.2	26.8	28753	463	72.5	14.3	92.9	84.9
	2	37442	86.5	28.1	29837	476	75.8	15.7	95.8	86.2
April	1	36755	89.0	26.0	30046	484	75.4	15.4	95.0	94.7
	2	38217	92.7	27.5	30501	489	76.0	15.8	98.0	90.1
June	1	36975	90.1	27.4	30035	487	75.6	15.3	96.4	89.0
	2	39083	93.7	27.7	30476	493	75.7	15.8	99.6	91.0
September	1	34969	86.4	24.4	29195	480	73.7	14.6	91.8	87.8
	2	32530	82.5	26.8	28959	475	74.2	14.4	84.6	86.1
Certified Value, ug/g		75000	130	34.6	35000	538	88	18.9	112	106
Standard Deviation		0.06	4	0.7	0.11	17	5	0.5	5	3
Month	Rep	Percent Recovery								
		AL	CR	CU	FE	MN	NI	PB	V	ZN
January	1	47	66	77	86	90	85	80	81	83
	2	47	66	83	86	89	86	86	84	83
February	1	49	66	77	86	88	85	81	84	81
	2	47	63	72	83	87	84	76	79	79
March	1	48	64	77	82	86	82	75	83	80
	2	50	67	81	85	88	86	83	86	81
April	1	49	68	75	86	90	86	82	85	89
	2	51	71	79	87	91	86	83	87	85
June	1	49	69	79	86	90	86	81	86	84
	2	52	72	80	87	92	86	84	89	86
September	1	47	66	70	83	89	84	77	82	83
	2	43	63	77	83	88	84	76	76	81
Average % Recovery		48	67	77	85	89	85	80	83	83
Standard Deviation		2	3	4	2	2	1	4	4	3

Table 1B. 2001 SRM 2709 (San Joaquin Soil) Recoveries (HNO₃ Extraction)

		Concentration, ug/g								
Month	Rep	AL	CR	CU	FE	MN	NI	PB	V	ZN
January	1	49033	96.5	27.3	32510	509	76.7	17.3	104	76.2
	2	46269	93.4	28.0	32047	503	76.9	17.2	99.3	75.3
February	1	44410	90.8	26.8	32180	506	76.3	17.0	94.5	76.6
	2	47289	94.2	27.3	31915	501	75.7	17.2	101	73.7
March	1	44726	90.6	27.1	31585	496	75.0	17.5	96.8	73.2
	2	45195	90.6	26.0	31305	490	74.2	16.3	95.1	71.8
April	1	49454	94.4	26.5	32678	512	74.5	17.5	100	77.0
	2	47333	93.4	26.5	32400	505	74.2	16.4	97.6	76.0
June	1	45809	89.5	25.2	31577	496	72.2	16.4	95.0	72.0
	2	47496	92.1	26.4	32032	501	72.8	16.8	96.9	73.4
September	1	46341	90.5	26.2	31727	495	72.5	16.6	97.2	72.2
	2	45364	90.0	25.9	31786	497	73.3	17.2	94.6	73.1
October	1	49350	94.1	28.2	32402	508	74.0	17.4	103	74.8
	2	43674	87.7	25.0	31284	493	72.4	15.9	90.6	72.3
December	1	49289	93.8	26.8	31998	501	72.9	17.3	101	74.8
Certified Value, ug/g		75000	130	34.6	35000	538	88.0	18.9	112	106
Standard Deviation		0.06	4	0.7	0.1	17	5	0.5	5	3

		Percent Recovery								
Month	Rep	AL	CR	CU	FE	MN	NI	PB	V	ZN
January	1	65	74	79	93	95	87	92	93	72
	2	62	72	81	92	93	87	91	89	71
February	1	59	70	77	92	94	87	90	84	72
	2	63	72	79	91	93	86	91	90	70
March	1	60	70	78	90	92	85	92	86	69
	2	60	70	75	89	91	84	86	85	68
April	1	66	73	76	93	95	85	92	89	73
	2	63	72	77	93	94	84	87	87	72
June	1	61	69	73	90	92	82	87	85	68
	2	63	71	76	92	93	83	89	86	69
September	1	62	70	76	91	92	82	88	87	68
	2	60	69	75	91	92	83	91	84	69
October	1	66	72	81	93	94	84	92	92	71
	2	58	67	72	89	92	82	84	81	68
December	1	66	72	77	91	93	83	91	90	71
Average % Recovery		62	71	77	91	93	84	90	87	70
Standard Deviation		3	2	3	1	1	2	3	3	2

Table 2A. Metal concentrations analyzed (at each sampling) in Certified Reference Material (NRCC) TORT-2 (Lobster hepatopancreas) compared to certified mean, maximum and minimum values for that material. [All values in micrograms per gram dry weight]

Date	Cadmium	Chromium	Copper	Lead	Nickel	Silver	Vanadium	Zinc
Jan 18 2000								
Feb 15 2000	25.8	1.04	101	0.11	2.31	5.31	1.55	161
March 22 2000	24.3	1.39	101	0.13	2.55	4.77	1.56	164
April 10 2000	23.9	0.67	94	0.26	2.14	6.37	1.61	154
Mean	24.7	1.03	99	0.17	2.33	5.48	1.58	160
STD	1.0	0.36	4	0.08	0.20	0.81	0.03	5

Certified Values

Mean	26.7	0.77	106	0.35	2.50		1.64	180
Max.	27.3	0.92	116	0.48	2.69		1.83	186
Min.	26.1	0.62	96	0.22	2.31		1.45	174

**Table 2B. Metal concentrations analyzed (at each sampling) in Standard Reference Material (NIST) 2976 (Mussel tissue) compared to certified mean, maximum and minimum values for that material.
[All values in micrograms per gram dry weight]**

Date	Cadmium	Chromium	Copper	Lead	Nickel	Silver	Vanadium	Zinc
June 19 2000	0.71	0.87	3.72	1.11	0.72	0.044	0.76	142
Sept 13 2000	0.63	0.63	3.68	0.97	0.63	0.029	0.64	129
Nov 9 2000	0.69	1.33	3.78	1.01	0.68	0.041	0.73	132
Dec 12 2000	0.68	0.40	3.86	1.02	0.70	0.051	0.74	133
Jan 9 2001	0.67	0.41	3.95	1.01	0.65	0.033	0.77	132
Feb 5 2001	0.72	0.47	3.81	1.09	0.68	0.033	0.78	138
March 5 2001	0.67	0.60	3.78	1.01	0.62	0.039	0.70	129
Arpril 10 2001	0.68	0.67	3.69	0.98	0.71	0.031	0.70	133
May 8 2001	0.67	0.68	3.67	0.94	0.66	0.025	0.70	131
June 12 2001	0.69	0.23	3.56	1.01	0.66	0.035	0.68	133
Sept 18 2001	0.68	0.45	3.64	1.02	0.63	0.029	0.65	134
Oct 15 2001	0.67	0.46	3.46	0.96	0.65	0.032	0.66	132
Dec 11 2001	0.65	0.42	3.52	0.96	0.60	0.028	0.63	130
Mean	0.68	0.59	3.70	1.01	0.66	0.035	0.70	133
STD	0.02	0.28	0.14	0.05	0.04	0.007	0.05	4

Certified Values

Mean	0.82	0.50	4.02	1.19	0.93	0.011		137
Max.	0.98	0.66	4.35	1.37	1.05	0.016		150
Min.	0.66	0.37	3.69	1.01	0.81	0.006		124

Table 3A. Concentrations, standard deviations and annual means describing sediment and environmental characteristics at the Palo Alto mudflat in 1999.

[Units are microgram per gram dry weight. STD is standard deviation of the two samples. SEM is standard error of the means for the year.]

Date	Aluminum (percent)		Iron (percent)		Manganese ($\mu\text{g/g}$)		Organic Carbon (percent)	Sand (percent)	Salinity (ppt)
	mean	std	mean	std	mean	std			
Jan 15	3.4	1.7	5.4	1.1	1013	33	1.43	11	18
Feb 25	4.9	0.1	7.6	0.2	997	13	1.45	9	18
March 22	4.7		6.9	0.2	1046	8	1.48	8	13
April 18	5.1	0.1	5.0	0.8	1238	5	1.55	4	16
May 19	3.7	0.1	3.7	0.03	685	4	1.13	29	23
June 16	3.9	0.1	3.7	0	722	1	1.22	32	22
Sept 13	3.4	0.1	3.3	0.03	909	4	0.98	68	
Nov 22	4.5	0.1	3.8	0	1310	3	1.26	39	
Dec 20	5.3	0.2	4.3	0	1596	9	1.48	5	24
Annual Mean: 1999	4.3		4.9		1057		1.33	23	19
SEM: 1999	0.2		0.5		96		0.06	7.1	1.5

Table 3B. Concentrations, standard deviations and annual means describing sediment and environmental characteristics at the Palo Alto mudflat in 2000.

[Units are microgram per gram dry weight. STD is standard deviation of the two samples. SEM is standard error of the means for the year.]

Date	Aluminum (percent)		Iron (percent)		Manganese ($\mu\text{g/g}$)		Organic Carbon (percent)	Sand (percent)	Salinity (ppt)
	mean	std	mean	std	mean	std			
Jan 1	5.4	0.04	4.5	0.02	1638	3	1.4	13	22
Feb 15	5.9	0.009	4.6	0.07	1380	22	1.5	17	18
March 22	5	0.4	4.3	0.05	979	12	1.4	16	10
April 10	5.2	0.2	4.4	0.04	1284	9	1.5	8	15
June 19	3.7	0.2	3.6	0.03	638	4	1.1	40	22
Sept 13	3.5	0.1	3.4	0.01	821	1	1	30	24
Nov 9	3.5	0.006	3.3	0.02	934	28	0.9	34	22
Dec 12	4.3	0.2	3.9	0.03	1216	3	1.2	39	24
Annual Mean: 2000	4.6		4.0		1111		1.25	25	20
SEM: 2000	0.3		0.2		116		0.08	4.4	1.8

Table 3C. Concentrations, standard deviations and annual means describing sediment and environmental characteristics at the Palo Alto mudflat in 2001.

[Units are microgram per gram dry weight. STD is standard deviation of the two samples. SEM is standard error of the means for the year.]

Date	Aluminum (percent)		Iron (percent)		Manganese ($\mu\text{g/g}$)		Organic Carbon (percent)	Sand (percent)	Salinity (ppt)
	mean	std	mean	std	mean	std			
Jan 9	4.9	0.3	4.2	0.1	1360	1.7	1.3	41	24
Feb 5	5.1	0.1	4.2	0.04	732	6.3	1.2	32	23
March 5	5.3	0.3	4.4	0.02	1300	7.7		29	20
April 10	5.6	0.1	4.3	0.007	1586	1.5	1.4	12	20
May 8	6.1	0.02	4.4	0.005	944	2.2		21	21
June 12	2.9	0.02	3.3	0.04	767	6.7	1.1	39	24
Sept 18	2.6	0.09	3.4	0.06	976	4.3	0.9	59	24
Oct 15	2.7	0.1	3.3	0.04	896	25.8	1	39	26
Dec 1	3.5	0.02	3.7	0.02	1358	0.9	1.3	16	24
Annual Mean: 2001	4.3		3.9		1102		1.17	32	23
SEM: 2001	0.5		0.2		101		0.07	4.9	0.7

Table 4A. Concentrations, standard deviations and annual means of trace elements in sediments in 1999 at the Palo Alto mudflat.

[Units are microgram per gram dry weight. STD is standard deviation of the two samples. SEM is standard deviation of the means for the year.]

Date	Cadmium		Chromium		Copper		Lead		Mercury	Nickel		Selenium	Silver		Vanadium		Zinc		Silver-HCl	
	mean	std	mean	std	mean	std	mean	std		mean	std		mean	std	mean	std	mean	std	mean	std
Jan 15	0.18	0.01	118	2	50	1.0	49		0.41	91	5.7	0.4	0.50	0.03	90	6.2	132	6	0.26	0.01
Feb 25	0.42	0.10	114	2	49	0.6	40	0.4	0.25	91	0.8	0.7	0.42	0.02	82	4.9	134	2	0.20	0
March 22	0.19	0.01	111	3	45	0.6	40		0.34	86	4.7	0.6	0.39	0.01	73	5.4	126	1	0.20	0.01
April 18	0.20	0.01	120	1	49	0.3	48	0.4	0.30	98	0.2	0.5	0.45	0.03	95	0.6	138	0.4	0.23	0.01
May 19	0.25	0	100	1	37	0.1	42	0.3	0.24	83	0.6	0.4	0.31	0	71	0.5	115	1	0.17	0.01
June 16	0.24	0.01	103	1	40	0.1	45	0.1	0.34	86	0.03	0.3	0.37	0.02	71	2.2	119	0.1	0.23	0.01
Sept 13	0.19	0	95	2.1	34	0.1	42	0.5	0.25	77	0.2	0.2	0.3	0	64	0.7	106	1	0.16	0
Nov 22			110	2	43	0.1	46	0.3	0.34	91	1.4	0.3			81	1.6	124	1	0.20	0.01
Dec 20			123	2	50	0.5	50	0.5	0.33	104	2.0	0.4			93	3.2	142	2	0.30	0
Annual Mean: 1999	0.24		110		44		45		0.31	90		0.4	0.39		80		126		0.22	
SEM: 1999	0.03		3.2		2.0		1.3		0.02	2.7		0.05	0.03		3.7		3.9		0.01	

Table 4B. Concentrations, standard deviations and annual means of trace elements in sediments in 2000 at the Palo Alto mudflat.

[Units are microgram per gram dry weight. STD is standard deviation of the two samples. SEM is standard deviation of the means for the year.]

Date	Cadmium		Chromium		Copper		Lead		Mercury	Nickel		Selenium	Silver		Vanadium		Zinc		Silver-HCl	
	mean	std	mean	std	mean	std	mean	std		mean	std		mean	std	mean	std	mean	std	mean	std
Jan 18			139	<i>0.6</i>	45	<i>0.1</i>	33	<i>0.3</i>		103	<i>0.3</i>				123	<i>1.6</i>	139	<i>1.5</i>	0.44	<i>0.01</i>
Feb 15			142	<i>0.7</i>	50	<i>0.4</i>	34	<i>0.7</i>		104	<i>2.1</i>				131	<i>0.3</i>	148	<i>2.4</i>	0.39	<i>0.01</i>
March 22			129	<i>5.9</i>	44	<i>2.2</i>	31	<i>0.8</i>		97	<i>1.5</i>				117	<i>7.8</i>	136	<i>3.6</i>	0.33	<i>0</i>
April 10			134	<i>4.9</i>	45	<i>1.4</i>	31	<i>0.5</i>		98	<i>0.6</i>				124	<i>7.1</i>	138	<i>1.1</i>	0.35	<i>0.01</i>
June 19			105	<i>3.6</i>	34	<i>0.7</i>	25	<i>0.03</i>		81	<i>0.3</i>				96	<i>3.7</i>	110	<i>2</i>	0.27	<i>0</i>
Sept 13			98	<i>2.7</i>	31	<i>0.6</i>	25	<i>0.7</i>		76	<i>0.2</i>				91	<i>4.8</i>	103	<i>0.5</i>	0.31	<i>0</i>
Nov 9			89	<i>1.4</i>	27	<i>0.4</i>	25	<i>0.3</i>		72	<i>0.9</i>				73	<i>0</i>	82	<i>0.3</i>	0.28	<i>0</i>
Dec 12			104	<i>3.5</i>	33	<i>1.4</i>	29	<i>0.3</i>		84	<i>1.2</i>				86	<i>3.5</i>	97	<i>0.6</i>	0.37	<i>0.01</i>
Annual Mean: 2000	#DIV/0!		118		39		29			89					105		119		0.34	
SEM: 2000	#DIV/0!		<i>7.3</i>		<i>2.9</i>		<i>1.3</i>			<i>4.5</i>					<i>7.5</i>		<i>8.5</i>		<i>0.02</i>	

Table 4C. Concentrations, standard deviations and annual means of trace elements in sediments in 2001 at the Palo Alto mudflat.

[Units are microgram per gram dry weight. STD is standard deviation of the two samples. SEM is standard deviation of the means for the year.]

Date	Cadmium		Chromium		Copper		Lead		Mercury	Nickel		Selenium	Silver		Vanadium		Zinc		Silver-HCl	
	mean	std	mean	std	mean	std	mean	std		mean	std		mean	std	mean	std	mean	std	mean	std
Jan 9			119	5.3	38	0.4	32	1.3		94	1.5				103	7.1	104	1.5	0.35	0
Feb 5			116	1.2	39	0.4	32	0.5		97	0.3				101	1.1	99	1	0.27	0
March 5			121	4.3	40	1.9	34	0.6		96	1.2				104	5.3	113	1.9	0.55	0
April 10			123	2.7	39	1.1	32	0.3		93	0.4				110	3.5	107	1.4	0.54	0.01
May 8			131	1.7	41	0.5	33	0.04		94	0.4				121	1.3	112	0.1	0.41	0
June 12			89	0.2	28	0.3	24	0.3		76	0.3				70	1.4	107	0.9	0.36	0
Sept 18			76	2.4	25	0.04	25	0.4		76	0.4				72	2.4	95	0.8	0.48	0.02
Oct 15			83	1.5	27	0.3	23	0.4		75	0.4				71	3.3	94	0.2	0.43	0.03
Dec 1			102	0.3	34	2.1	27	0.5		84	0.8				81	1.9	122	0.6	0.47	0
Annual Mean: 2001	#DIV/0!		107		35		29			87					93		106		0.43	
SEM: 2001	#DIV/0!		6.6		2.1		1.4			3.1					6.4		3.0		0.03	

Table 5A. Concentrations, standard error of means (SEM) and annual means of trace elements in the soft tissues of the clam *Macoma balthica* in 1999 at the Palo Alto mudflat.

[All units microgram per gram soft tissue dry weight. Wt. 25mm is the condition index or weight in milligrams of a 25 mm shell length clam. SEM are standard deviations of the mean from 6-14 replicate analyses of composite samples.]

Date		Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Vanadium	Zinc	Wt. 25mm
Jan 15	mean	0.20	5.1	35	4.7	0.29	6.1	4.7	3.4	4.4	337	92
	sem	0.03	0.4	4	0.4	0.01	0.4	0.2	0.8	0.4	30	
Feb 26	mean	0.18	3.6	42	3.1		5.2		4.2	3.5	412	84
	sem	0.02	0.3	3	0.3		0.4		0.5	0.3	41	
March 22	mean	0.17	2.5	32	2.1		4.0		2.5	2.2	340	112
	sem		0.2	2	0.1		0.1		0.3	0.1	14	
April 18	mean		1.9	31	1.8	0.15	3.5	3.3	2.5	1.6	328	126
	sem		0.2	4	0.2	0.02	0.1	0.1	0.5	0.1	21	
May 19	mean		1.8	29	1.3		3.3		2.8	1.6	417	103
	sem		0.1	2	0.2		0.2		0.2	0.1	25	
June 16	mean		1.7	32	2.2		3.8		2.9	1.6	361	133
	sem		0.2	2	0.7		0.1		0.3	0.2	27	
Sept 13	mean		2.3	43	2.5	0.30	4.4	5.3	4.6	2.2	339	101
	sem		0.3	2	0.2	0.02	0.2	0.2	0.3	0.3	30	
Nov 23	mean		3.3	21	3.7		4.2		4.7	2.8	321	100
	sem		0.6	1	0.6		0.4			0.4	38	
Dec 20	mean		4.2	38	4.0	0.31	5.3	5.5	5.1	3.8	262	102
	sem					0.02		0.2			25	
Annual Mean		0.18	2.9	34	2.8	0.26	4.4	4.7	3.6	2.6	346	106
SEM		0.01	0.4	2	0.4	0.04	0.3	0.5	0.3	0.4	16	5

Table 5B. Concentrations, standard error of means (SEM) and annual means of trace elements in the soft tissues of the clam *Macoma balthica* in 2000 at the Palo Alto mudflat.

[All units microgram per gram soft tissue dry weight. Wt. 25mm is the condition index or weight in milligrams of a 25 mm shell length clam. SEM are standard deviations of the mean from 6-14 replicate analyses of composite samples.]

Date		Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Vanadium	Zinc	Wt. 25mm
Jan 18	mean	nd	3.6	30	3.1	0.31	4.8	5.9	3.3	3.0	313	
	sem		0.3	2	0.3	0.03	0.1	0.1	0.5	0.2	21	
Feb 15	mean	0.31	3.0	37	1.2		4.5		4.0	3.0	429	99
	sem	0.66	0.0	0	0.2		3.5		0.1	0.3	20	
March 22	mean	0.43	3.6	48	1.2		5.5		5.2	3.9	490	104
	sem	0.04	0.4	5	0.1		0.5		0.9	0.5	32	
April 10	mean	0.38	3.0	21	0.9	0.36	4.0	4.9	1.9	2.9	241	164
	sem	0.02	0.2	2	0.1	0.20	0.2	0.2	0.4	0.2	12	
June 19	mean	0.14	2.0	19	0.8	0.18	3.1	3.4	1.3	1.2	207	187
	sem	0.01	0.3	3	0.1	0.01	0.2	0.1	0.2	0.1	11	
Sept 13	mean	0.22	2.7	35	1.2	0.27	4.6	3.8	2.5	1.9	195	120
	sem	0.01	0.2	1	0.1	0.02	0.2	0.5	0.3	0.1	15	
Nov 9	mean	0.40	3.1	29	1.2		4.2		2.2	2.8	148	162
	sem	0.11	0.7	5	0.2		0.6		0.3	0.5	24	
Dec 12	mean	0.30	2.2	37	1.3		4.4		3.4	2.7	212	105
	sem	0.02	0.2	2	0.1		0.2		0.6	0.2	17	
Annual mean		0.31	2.9	32	1.4	0.28	4.4	4.5	3.0	2.7	279	134
SEM		0.04	0.2	3	0.3	0.04	0.2	0.6	0.4	0.3	43	13

Table 5C. Concentrations, standard error of means (SEM) and annual means of trace elements in the soft tissues of the clam *Macoma balthica* in 2001 at the Palo Alto mudflat.

[All units microgram per gram soft tissue dry weight. Wt. 25mm is the condition index or weight in milligrams of a 25 mm shell length clam. SEM are standard deviations of the mean from 6-14 replicate analyses of composite samples.]

Date		Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Vanadium	Zinc	Wt. 25mm
Jan 9	mean	0.32	2.6	36	1.2	0.34	4.3	6.7	3.8	3.0	279	93
	sem	0.02	0.2	1	0.1	0.04	0.2	0.5	0.6	0.2	19	
Feb 5	mean	0.31	4.0	32	1.2		4.9		3.7	3.5	350	104
	sem	0.02	0.4	3	0.1		0.3		0.6	0.3	23	
March 5	mean	0.29	4.0	32	1.3		4.8		2.6	3.4	333	98
	sem	0.02	0.3	2	0.1		0.3		0.3	0.3	14	
April 10	mean	0.24	3.0	24	1.0	0.29	4.1	4.5	1.9	2.6	306	125
	sem	0.02	0.2	4	0.1	0.03	0.4	0.4	0.3	0.2	26	
May 8	mean	0.17	1.9	21	0.7		3.1		1.5	1.5	266	146
	sem	0.01	0.2	2	0.1		0.3		0.3	0.2	13	
June 12	mean	0.14	1.5	22	1.0	0.23	2.9	3.6	1.3	1.0	229	134
	sem	0.01	0.1	1	0.1	0.01	0.1	0.2	0.1	0.1	16	
Sept 18	mean	0.26	2.4	37	1.5	0.31	5.0	3.5	3.5	2.7	247	121
	sem	0.01	0.1	1	0.1	0.03	0.1	0.2	0.2	0.1	21	
Oct 15	mean	0.21	1.7	30	1.2		4.2		3.2	1.9	197	111
	sem	0.01	0.1	3	0.0		0.1		0.4	0.1	14	
Dec 11	mean	0.34	2.7	44	1.6		6.2		5.0	3.0	273	95
	sem	0.03	0.1	3	0.1		0.5		0.4	0.2	26	
Annual mean		0.25	2.7	31	1.2	0.29	4.4	4.6	2.9	2.5	276	114
SEM		0.02	0.3	3	0.1	0.02	0.3	0.7	0.4	0.3	16	6

Table 6. Annual mean copper (Cu) concentrations in clams and sediments at Palo Alto: January 1977 through December 2001.

[Values are annual means from 7 to 12 collections per year and standard errors of those means for the year. Means are calculated between January and December. Units are microgram per gram dry weight of soft tissue for clams (*Macoma balthica*) and microgram per gram dry weight for sediment.]

Year	Copper in sediment		Copper in clams
	HCI	Total	
1977	28±6	45±13	130±23
1978	42±11	57±13	187±104
1979	55±13	86±18	248±114
1980	47±5	66±9	287±66
1981	48±7	57±22	206±55
1982	35±4	34±24	168±35
1983	22±9	38±21	191±48
1984	26±10	40±16	159±55
1985	27±3	45±7	138±22
1986	24±3	49±9	114±49
1987	21±3	47±6	95±25
1988	27±3	53±5	53±24
1989	23±6	44±13	35±10
1990	23±2	51±4	35±11
1991	25±2	52±5	24±8
1992	27±6	52±5	46±14
1993	21±3	43±7	60±14
1994	19±2	45±4	59±12
1995	19±2	44±5	61±16
1996	19±2	43±4	71±11
1997	18±1	43±3	32±7
1998	20±1	46±2	35±4
1999	18±1	44±2	34±2
2000	18±1	39±3	32±3
2001	17±1	35±2	31±3

Table 7. Annual mean silver (Ag) concentrations in clams and sediments at Palo Alto: January 1977 through December 2001.

[Values are annual means from 7 to 12 collections per year and standard errors of those means for the year. Means are calculated between January and December. Units are microgram per gram dry weight of soft tissue for clams (*Macoma balthica*) and microgram per gram dry weight for sediment.]

Year	Silver in sediment	Silver in clams
1977	0.65 ± 0.59	87 ± 21
1978	1.39 ± 0.35	106 ± 17
1979	1.62 ± 0.28	96 ± 29
1980	1.28 ± 0.38	105 ± 24
1981	1.41 ± 0.15	63 ± 18
1982	0.74 ± 0.21	45 ± 13
1983	0.56 ± 0.26	56 ± 11
1984	0.64 ± 0.20	57 ± 18
1985	0.78 ± 0.14	58 ± 6
1986	0.61 ± 0.14	50 ± 20
1987	ND	55 ± 18
1988	ND	20 ± 10
1989	ND	11 ± 4
1990	0.39 ± 0.09	7.7 ± 3.4
1991	0.25 ± 0.07	3.3 ± 2.0
1992	0.35 ± 0.11	5.9 ± 1.9
1993	0.36 ± 0.09	6.9 ± 3.2
1994	0.46 ± 0.07	5.4 ± 1.1
1995	0.27 ± 0.05	5.5 ± 1.2
1996	0.24 ± 0.06	7.5 ± 1.6
1997	0.34 ± 0.04	3.6 ± 1.0
1998	0.34 ± 0.04	3.3 ± 0.6
1999	0.22 ± 0.01	3.6 ± 0.3
2000	0.34 ± 0.02	3.0 ± 0.4
2001	0.43 ± 0.03	3.0 ± 0.4